# Mineralogy and Trace Elements of the Cretaceous Greymouth Coals and their Combustion Products

*Volume I: Text*

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# Abstract

Understanding the spatial distribution trends and modes of occurrence (e.g. physical and chemical forms) of trace elements in coal seams is a key factor to any assessment of their potential impacts on the environment and human health. Two Cretaceous coal seams (E and Main) from the Greymouth coalfield, which is one of the most important coal-producing basins in New Zealand, were chosen for this study. The main objectives of this study are: (a) to delineate the concentration and spatial distribution of trace elements in the two coal seams, (b) to determine the modes of occurrence of trace elements in these coals, (c) to develop models of how trace elements from the Greymouth coalfield behave during combustion, and to assess the potential environmental impacts from mining and combustion of these coals.

Examination of 184 samples from both the E and Main seams as well as 94 Main seam-composite samples from a drilling coal quality database, showed that both seams are characterized by great thickness (up to 35m) and low ash yield (<0.6% in some cases). The coals are laterally discontinuous as a result of both faulting and rapid sedimentary facies changes. In general a reverse relationship exists between ash content and coal thickness. Modeling of the lateral variations of major elements in the coal seams identified two possible inorganic sources for these coals. Furthermore, morphological features of minerals (quartz and clays) and the secondary mobilisation of liptinitic materials suggest that the Greymouth coals may have undergone extensive leaching in both peat and post-burial stages. Based on the physical and chemical evidence, a model for the leaching mechanisms has been proposed to explain how the leaching processes may have operated in the Greymouth coals. The major points of this model are:

1. Abundant organic acids in peat stage favor plant degradation and produce ~90% of the inorganics as exchangeable ions, which are active and readily leachable.
2. With rising temperature (30 to 70°C) in the lignite stage, minerals partly dissolve and become mobile. The porous structure of lignite allows exchangeable ions to be leached out of the coalbed through incipient cleats and/or micropores.
3. In the subbituminous to bituminous stages (70 to 170 °C), organically bound

inorganic elements are expelled due to organic matter breakdown and leached away by percolating solutions through cleat networks.

Concentrations of all trace elements of interest are relatively low compared with many overseas coals of similar rank and age, although a few environmentally sensitive elements (As, Pb, Cl) are locally enriched. Due to the low concentrations in the coal beds studied, it is impossible to determine the modes of occurrence of trace elements by direct identification and examination of the host minerals. Thus, a group of direct (SEM-EDXA, microprobe and INAA analysis of trace elements in minerals) and complimentarily indirect (float-sink test, sequential leaching tests, inter-elemental correlations) techniques and approaches have been employed to determine the modes of occurrence of trace elements in the Greymouth coals. The following results have been obtained:

(1) Most trace elements including some hazardous air pollutants (HAPs) (As, Be, Cr, Hg, Sb and U) are predominantly associated with minerals (mainly clays) in the coal.

(2) Some trace elements (B, Br, Cd, Cl, Co, Ni and Se) are bound organically or as sub-micron-sized minerals intimately admixed in the organic matrix.

(3) REE, Th and Y are mainly associated with phosphates.

(4) The mineral crocoite ($PbCrO_4$) is identified for the first time in coal and is a major host for Pb and $Cr^{6+}$.

(5) Some elements usually only associated with sulphides (e.g., As, Hg, Sb and Zn) are mainly within clays in the Greymouth coal seams studied.

In addition to examining the distribution and mode of occurrence of trace elements in the Greymouth coal seams, their combustion characteristics were also investigated. The distribution and partitioning of trace elements during combustion was as follows:

(1) Most trace elements including some HAPs (As, Co, Cr, Ni, Pb) are predominantly partitioned in the bottom ash, especially in three major phases (Fe-oxides, Si-Al-O glass, and Fe-bearing silicate). As and Mn are predominantly partitioned in the

Fe-oxides; most other trace elements are partitioned between the other two phases.

(2) In contrast, S and Hg, and to a lesser extent, B, Cd and Cl, are chiefly partitioned in the flue gas fraction. However, a proportion of Hg (<10%) is probably absorbed onto the surface of fly ash particles, and this fraction of Hg may be freely released into the soil or water.

(3) Although the low ash Greymouth coals have the advantage of generating small volumes of solid combustion ashes, one of the consequences is that combustion can enrich the trace elements in the ashes very significantly. For example, B, S, and Cl were enriched to 1100 ppm, 4.4% and 2000 ppm, respectively.

Due to the low concentrations of toxic metals in the Greymouth coals and their combustion ashes, no major adverse potential environmental impacts would be expected based on the knowledge gained in this study. But it is prudent to further investigate the release of some toxic metals in the surface and subsurface waters in the coal mining areas and the long-term stockpile sites in the future.

# Table of Contents

## *Volume I: Text*

## Chapter 3 Mineralogy and Geochemistry

## Chapter 4 Trace Elements in Coal

## Chapter 5 Combustion Behaviour of Elements

## Chapter 6 Main Conclusions

Li, Z., Moore, T.A. and Weaver, S.D., 1999a. Mineralogy and geochemistry of Cretaceous Main Seam coal, Greymouth, West Coast, New Zealand. Proceedings of a New Zealand Energy Road Map - Vision for 2020 and 8th New Zealand Coal Conference, Wellington, pp. 183-199.

Li, Z., Moore, T.A. and Weaver, S.D. and G. Gillard, 2000. Thick and delicious: the story of Greymouth coals. Proceedings of 17th Annual Conference of The Society for Organic Petrology (TSOP), Indiana University, Bloomington, pp. 56-58.

## Back Pocket

Li, Z., Moore, T.A. and Weaver, S.D., 2001a. Leaching of inorganics in the Cretaceous Greymouth coal beds, South Island, New Zealand. International Journal of Coal Geology, 47 (3-4), pp. 235-253.

Li, Z., Moore, T.A., Weaver, S.D. and Finkelman, R.B., 2001b. Crocoite: an unusual mode of occurrence of lead in coal. International Journal of Coal Geology, 45 (2), pp. 289-293.

# *Volume II: Tables, Figures & Appendices*

## List of Figures

### Chapter 1



### Chapter 3

## Chapter 4

## Chapter 5

## List of Tables

### Chapter 2



### Chapter 3

## Chapter 4

## Chapter 5

# List of Appendices

# List of abbreviations used in the text

| | |
|---|---|
| AmAc | ammonium acetate ($CH_3COONH_4$) |
| ASTM | American Society for Testing and Materials |
| CVAA | cold vapour atomic absorption |
| DH | drillhole |
| DL | detection limit |
| EMP | electron microprobe analysis |
| GCOL | Greymouth Coal Operating Limited |
| HAP | hazardous air pollutant |
| HCl | hydrochloric acid (HCl) |
| HF | hydrofluoric acid (HF) |
| $HNO_3$ | nitric acid ($HNO_3$) |
| HREE | heavy rare earth elements |
| HTA | high temperature ash |
| ICP-AES | Inductively coupled plasma-atomic emission spectrometry |
| ICP-MS | Inductively coupled plasma-mass spectrometry |
| IGNS | Institute of Geological and Nuclear Sciences Ltd. |
| INAA | Instrumental neutron activation analysis |
| LLD | lower limits of detection |
| LREE | light rare earth elements |
| LTA | Low temperature ash |
| NIST | U.S National Institute of Standards and Technology |
| REE | rare earth elements |
| SARM | South Africa Reference Materials |
| SEM | Scanning electron microscope |
| SEM-EDXA | Scanning electron microscope with energy-dispersive X-ray Spectrometers |
| XRD | X-ray diffractometer |
| XRF | X-ray fluorescence (WD-XRF) spectrometer |
| WD-XRF | wave-length dispersive X-ray fluorescence (WD-XRF) spectrometer |

# Chapter 1

# Chapter 1 Introduction

## 1.1 The Purpose of This Study

The Greymouth coalfield is one of the most important coal-producing basins in New Zealand. Virtually all bituminous coals in New Zealand occur in this area and the adjacent Buller coalfield. Thus, coal mining is one of the most important industries in this region. The purpose of this study is to understand the trace element concentrations, their modes of occurrence and the geochemical controls on their distribution in the Greymouth coals. This knowledge will allow potential environmental issues associated with coal combustion to be addressed.

Coal is likely to remain a major energy source for most countries, including the US and China, in the foreseeable future. Although coal is comprised predominantly of organic matter, inorganic constituents are important and can ultimately determine how the coal will subsequently be utilised.

Inorganic constituents in coal occur as either discrete mineral grains or organically bound elements. With increasing environmental awareness, concerns on the effects of the release of toxic metals from coal mining and coal combustion has resulted in numerous studies. Potential health and environmental impacts caused by some hazardous trace elements in coal (such as As, Cl, Hg, Sb, and the minor elements B, S) have been the focus of these studies. As a preventive measure, the US Clean Air Act Amendments of 1990 (U.S. Statutes at Large, 1990) specifically identified 12 potentially hazardous air pollutants (HAPs) that may be released during coal combustion. The HAPs are As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se and U. Some of the HAPs have been noted in New Zealand coal seams (Sim and Lewin, 1975; Sim, 1977; Mackay and Wilson, 1978; Newman, 1988; Purchase, 1985, 1989, 1993) as well as combustion products from these coals (Clemens et al., 1997).

It is important to know what is released from New Zealand coals upon combustion because many New Zealand towns and cities burn coal. In particular, Environment Canterbury has shown that domestic solid fuel burning (including both coal and wood) produces >90% of the suspended particulate material with diameter of less than 10 μm (referred to as $PM_{10}$) (**Fig. 1.1**) pollution during winter months (The Winter Report – Christchurch, 2001). Hales et al. (1999) reported that particulate ($PM_{10}$) pollution contributes to 70 deaths a year from respiratory problems. Moreover, the proposed ratification and commitment to the Kyoto Protocol on Climate Change by the New Zealand Government will probably give rise to tighter regulations on the emission of air pollutants from coal combustion in both industrial and domestic uses. Both national and international pressures will require higher levels of understanding on what is emitted from coal when it is burned.

Understanding controls on trace element distribution in coal may also provide crucial information related to acid mine drainage. For example, high concentrations of metals in acid mine run-offs might be predicted before mining, allowing preventative actions to be taken before coal extraction. Elevated levels of metals from acid mine drainage from the downstream areas, West Coast, New Zealand (Leon and Anstiss, 2002) would be better understood with a good knowledge of trace element distribution in these coals.

Although there are numerous studies performed overseas on trace elements in coal, only a limited amount of work has been done in New Zealand on trace elements in coal, and most of these studies were focused on the Waikato subbituminous coals (Sim and Lewin, 1975; Sim, 1977; Mackay and Wilson, 1978). Virtually no known systematic studies exist for trace elements on the West Coast coals. One exception to this is a study by Newman (1988) who discussed Ba, Ni and Sr. No study on trace element behaviour upon combustion has been conducted. Thus, we still have little understanding about the trace elements (especially HAPs) in these coals and their combustion products, especially their origin, modes of occurrence, distribution in coal and combustion products, their behaviour and fate during the combustion, as well as their potentially deleterious effects

on the environment. This study is designed specifically to address all these issues and to clarify the uncertainty surrounding the potential environmental impacts of trace elements in the Greymouth coals and their combustion by-products.

## 1.2 General Geology

The Greymouth coalfield is situated about 10 km north of Greymouth, the largest town on the West Coast of the South Island, New Zealand (**Fig. 1.2**). Greymouth coalfield covers an area of approximately 200 sq. km and lies on the south end of the Paparoa Range (**Fig. 1.3**), west of the Alpine Fault. Both the southern and eastern margins are broadly defined by the Grey River while the western margin extends offshore into the Tasman Sea (Bowman, 1982). Greymouth coalfield was first discovered by Thomas Brunner in 1848. Morgan (1911) did some basic geological work. Detailed survey of the coalfield began in 1936 and culminated in the New Zealand Geological Survey Bulletin 45 (Gage, 1952), which was a milestone in terms of determining coal occurrence and structures associated with coal seams.

In a comprehensive basin study of the West Coast region, Nathan et al. (1986) reported that coal measure sedimentation began in the latest Cretaceous but was restricted to four separate fault-bounded basins ranging from latest Cretaceous to Paleocene age. These four basins in the Late-Cretaceous were Pakawau and Greville Basins in the north near Nelson, the Paparoa Trough from the Buller to Greymouth regions, and finally the South Westland Embayment in the south. Whilst the South Westland Embayment was overlain by a transgressive marine succession, the other three basins were remote from the sea at this time and contain only non-marine sediments during the Cretaceous. This study deals with the Greymouth coalfield, which is a small part of the Paparoa Trough basin.

Although the present topography has only been formed over the last 2 million years, the N-NNE trending structural features (the Southern Alpine Fault, the Cape Foulwind Fault zone, the Grey-Inangahua Depression, and the Paparoa fault zone) appear to control not only the orientation of several Late-Cretaceous to Pliocene sedimentary basins, but also

the sedimentation during the last 80 million years (Nathan et al., 1986). Evidence suggests that individual faults have been reactivated in response to changing stress regimes (Laird, 1968, 1980).

With respect to the present topography, the western onshore part of the Greymouth coalfield is characterised by steep rugged terrain which rises sharply from the Tasman Sea and occurs as a series of mountain ranges. The crest of the Paparoa Range forms the backbone of the Greymouth coalfield and reaches a maximum elevation of 1100 m at Mt. Watson in the north. The eastern flanks of the Paparoa Range form a steep east-facing scarp. The interior of the coalfield is uniformly steep and rugged with not much flat land except along small strips near stream beds and terraces. Indeed, <20% of the coalfield is comprised of flat lowland and much of this is poorly drained and swampy (Bowman, 1984). Whereas the eastern part of the coalfield is drained by many small streams, the northern and central areas are drained by the Ten Mile and Seven Mile creeks which flow directly west into the Tasman Sea. The south-west part of the coalfield is drained by Coal Creek and McLean Creek which join the Grey River just above its confluence with the sea (Bowman, 1984).

Numerous coal seams occur in different sedimentary horizons within the Greymouth coal basin. However, all economically important West Coast coals are restricted to either the Paparoa (Late Cretaceous to Paleocene) or the Brunner (Eocene) Coal Measures (**Fig. 1.4**). The former contains the greatest coal reserve and the occurrence of the Paparoa Coal Measures in the Greymouth coalfield is shown in **Fig. 1.3.** The Brunner Coal Measures rest unconformably on either Paleozoic basement Greenland Group, mid-Cretaceous Pororari Group, or Paparoa Coal Measures (see Nathan et al., 1986, for more details). In contrast, the Paparoa Coal Measures span the Cretaceous-Tertiary boundary (Ward, 1997) and rest unconformably on either basement Greenland Group or mid-Cretaceous Pororari Group rift sediments (Gage, 1952, Laird, 1980). In the Greymouth Coalfield, seven formations and members (**Fig. 1.4**) were recognised within the Paparoa Coal Measures (Gage, 1952). These are: Jay, Ford, Morgan, Waiomo, Rewanui, Goldlight and Donollie Formations. Although several members (Morgan, Rewanui and

Brunner Coal Measures) contain sizeable and minable seams, the Rewanui has the greatest coal resources and mining potential. Because of the great economic value of the Rewanui coal seams and the availability of samples, this section was chosen for this study.

## 1.3 Study Area

The Greymouth coalfield has been broadly divided into two sectors: the Rapahoe Sector in the west and the Mt Davy Sector in the east. However, this study is only focused on two specific seams, the Main and E seams, occurring within the Rewanui Coal Measures. The Main seam (with thicknesses in excess of 35 m) occurs in the upper Rewanui Coal Measures (**Fig. 1.4**) and the study area of the Main seam covers an area of approximately 9 sq. km in the Rapahoe Sector (**Fig. 1.5**). The E seam (with thicknesses to about 14 m) also occurs in the upper part of the Rewanui, in the Rapahoe Sector. The study area for the E seam covers an area of approximately 1 sq. km in the Strongman #2 Mine (**Fig. 1.5**). There are three major reasons for focusing on these two seams. Firstly is their economic importance. Both seams occur in the Rewanui Coal Measures, which not only contains 80% of the coal resources remaining in the coalfield (Bowman, 1984) but also represents most of the coal production at present in this region. This production trend is likely to continue for the foreseeable future. Secondly, both seams are geologically and geochemically interesting with great thicknesses but very low ash content (often <3%). Looking into the low ash nature of these coals and the possible mechanism(s) responsible for this has geological significance, and may provide insight or explanation to other similar coals elsewhere. Thirdly, the accessibility of coal samples complimented with sufficient geological and geophysical data permitted a detailed study to be conducted.

In the Strongmam mine area, multiple seams occur and are informally termed "E", "D", "C", and "B" seams in a descending fashion. An angular relationship between the Goldlight mudstone-Rewanui Coal Measures contact and the "E", "D" and "C" seams has been noted (Hope, 1963; Thorburn, 1981). Thorburn (1981) observed a strong NW-SE trend in thickness of the E and D seams and the northern part of the C seam.

Southwards, the E and D seams thin out and are replaced by the C and B seams. The coal seam architecture in the E seam basin is illustrated in **Fig. 1.6**. However, the E seam is present over the whole study area, and only thins out further southwards in the study area.

## 1.4 Relevant Previous Work to This Study

A number of studies on the Greymouth coalfield have been made. However, all of them have been focused on either mapping, sedimentology, palynology or tectonics. For example, since Gage (1952) and Nathan (1978) mapped the Greymouth coalfield, Bowman (1982, 1984) examined the coal resources and outlined the structural and sedimentology factors. Jane Newman's studies (e.g. Newman, 1985, 1987a) have focused on coal properties (rank, volatile matter, reflectance) and paleoenvironments. Nathan et al. (1986) gave a comprehensive review of sedimentary basin development in the West Coast region by synthesizing stratigraphic columns as well as structural and seismic information available in 1986. Work by Nigel Newman (1988) investigated mineral matter of West Coast coals but emphasized the Tertiary Brunner Coal Measures, although the Paparoa coals in the Rapahoe areas were also discussed. Moore (1995) examined the microscopic coal types of the Main seam and "D" seam (in Strongman area). Moore (1996a) and Ward (1997) conducted palynological and sedimentological studies in the Paparoa Coal Measures. Moore (1996b) and Ferm and Moore (1997) examined the rock and coal type distribution in the coalfield. Sherwood et al. (1992) investigated the depositional controls on the Greymouth coal basin. Kamp et al. (1999) reconstructed the paleotemperatures experienced during burial of the Late Cretaceous and mid-Eocene coal-bearing sequences using fission track and vitrinite reflectance.

With mining technology advances in the last a few decades, the substantial sub-surface coal resources in the Greymouth coalfield have become an economic reality. Although the above-mentioned studies examined the Greymouth coalfield in broad terms, no systematic study has been undertaken to investigate the mineralogy and geochemistry of these coals except Newman's (1988) study, which, as pointed out earlier, was limited

mostly to the Brunner Coal Measures. Virtually no trace element geochemical study has been done on either the Main or E seams.

## 1.5 The Scope and Objectives of This Study

The scope of this work is to undertake a detailed case study on both the Main and E seam coals to obtain an understanding of the coal mineralogy, the major and trace element geochemistry, and to deduce how these coals came to have such low ash contents. More importantly, in order to address the environmental issues associated with the mining and utilisation of these coals, this study is specifically focused on the trace elements, their distribution and modes of occurrence as well as their origin. Finally the combustion behaviour of the trace element, such as their fate and partitioning in different combustion products, have been determined and their potentially environmental implications are also discussed.

Therefore, this thesis has the following objectives:

(1) To delineate the spatial distribution of ash yield and its relationship to coal seam geometry, and to identify the geochemical controls which govern the distribution of inorganics in the Greymouth coal seams,

(2) To establish and delineate the modes of occurrence of the trace elements in the coal, and quantify the percentages of these occurrences for each specific trace elements,

(3) To model the combustion behaviour of selected trace elements, which would include their fate and partitioning characteristic. Finally, to assess any potential environmental impacts of trace elements in the Greymouth coals and their combustion.

## 1.6 Publications Related to This Thesis

Parts of this thesis have already been published—these papers are either present in the back of Volume I or included in the back pocket of Volume I and are as follows:

- Li, Z., Moore, T.A. and Weaver, S.D., 1999a. "*Mineralogy and geochemistry of Cretaceous Main Seam coal, Greymouth, West Coast, New Zealand*", has been incorporated into Chapter 3, Sections 3.3 and 3.4.

- Li, Z., Moore, T.A. and Weaver, S.D. and G. Gillard, 2000. *Thick and delicious: the story of Greymouth coals*. Proceedings of the 17th Annual Conference of The Society for Organic Petrology, Indiana University, Bloomington, pp. 56-58.

- Li, Z., Moore, T.A. and Weaver, S.D., 2001a. "*Leaching of inorganics in the Cretaceous Greymouth coal beds, South Island, New Zealand*", has been incorporated into Chapter 3, Sections 3.1 to 3.7.

- Li, Z., Moore, T.A., Weaver, S.D. and Finkelman, R.B., 2001b. "Crocoite: an unusual mode of occurrence of lead in coal", has been integrated into Chapter 4, Section 4.5.

# Chapter 2

# Chapter 2 Sample Programme and Analytical Methodologies

## 2.1 Sampling Programme

As discussed in Chapter 1, this study only focuses on the Main seam in the Rapahoe Sector and the E seam in the Strongman #2 Mine (**Fig. 1.5**). Both seams occur in a similar stratigraphic interval within the Rewanui Member of the Paparoa Coal Measures (**Fig. 1.4**).

In order to understand the geological and geochemical factors that control the spatial distribution of trace elements in this region, two seams were sampled. A total of 184 samples (89 from the E seam and 95 from the Main seam) were collected (**Appendix 1**). These samples consisted of coal, inorganic partings as well as roof and floor sediments. The samples came from a combination of boreholes as well as underground and opencast mine sites.

The E seam samples were taken from six different locations (four underground and two opencast locations) of the current workings in the Strongman No. 2 Mine, covering an area of approximately 1x1 $km^2$. The sample site locations are given in the index map **Fig. 1.5.** Before sampling, the weathered surface was trimmed, so a fresh coal seam surface was exposed for sampling. On average, 15 ply samples were taken from each sample site following standard sampling procedures of American Society for Testing and Materials (ASTM, 1997). Therefore, this is a 'pilot study' limited by funding.

Because the Main seam does not outcrop at the surface, samples of the Main seam were collected from drill cores stored at Greymouth. The sampled drillholes are DH 703 and 755 in the north part of study area, DH 819 and 836 and one underground site "MU" from the SE of the study area. The sample locations are shown in **Fig. 1.5**. Because of the

limitation of sampling from core, block samples were taken based on macroscopic appearance of the coal. This sampling methodology has been used elsewhere in New Zealand (Shearer, 1992; Shearer and Moore, 1994) and overseas (Moore and Ferm, 1988, 1992). Before sampling, each core was macroscopically logged noting the appearance of sediment and bright charcoal layers. The coal itself was described using the proportion of vitrain bands and the lustre of the intervening attrital layers as a guide. This system for Greymouth coals is described by Ferm and Moore (1997).

Every sample represents a specific portion (of thickness) of the Main seam in terms of lithology and depth. Sample depth represents the midpoint of a length of core representing a particular sampled interval.

Among the 95 samples of the Main seam, 78 samples, including coal, associated partings, roof and floor sediments, were collected from two cores (DH 703 and 755) in the north part of the study area. Thirty-four samples came from an unsplit thick seam intersection (DH 703) of total thickness of 24 m; whereas 44 samples came from where the seam was split into an upper (10.87 m thick) and a lower (8.22 m thick) seam. In addition, samples were taken from associated roof (2.59 m), inter-seam inorganic partings (3.17 m), and floor rocks (1.65 m) in DH 755.

There were also 17 out of the 95 samples taken from other two drillholes (DH 819 and 836). Finally, at the underground sampling site, "MU" in the southeast part of the Main seam study area, samples were taken. Only the upper split of the Main seam have been sampled for these three locations (MU, DH 819 and 836) due to the limitations of access to the lower split of the Main seam in these areas.

All sample information from both the Main and E seams are given in **Appendix 1**. If applicable, sampled depth or sampled thickness and ash content of sampled intervals are also given in **Appendix 1**. For geographic positions of sample locations, refer to **Fig. 1.5**.

To determine trace element behaviour upon combustion, each combustion test requires at least 35 kg of feed coal. Unfortunately, it was not possible to obtain this size of sample for the Main seam because only core samples were available. Therefore, it was decided to sample a stratigraphically similar coal seam (E seam) with equivalent coal quality (low ash and sulphur) from the Strongman No. 2 Mine. Three coal channel samples were taken in accordance with ASTM standard D4596-86 (ASTM, 1995) from two different underground locations (P532A, 2A-2B) but in the same seam ("E" seam) from Strongman No. 2 Mine. The sampling location is given in **Fig. 1.5**. Sample P532A was taken from the northwest margin of Strongman No. 2 Mine site and represents the whole seam, whereas 2A and 2B were taken from another underground site close to the centre of the mine. Samples 2A and 2B represent the upper and lower portion of the E seam respectively. The samples were sent to CRL Energy Limited in Lower Hutt for combustion testing.

## 2.2 Sample Preparation and Crushing

### 2.2.1 Crushing

Before crushing, representative blocks were selected, moulded, and polished for petrographic examination. The remaining coal was then wrapped in plastic bags and crushed to small fragments by hammer, and subsplit. One subsplit was further reduced to <60 μm in a tungsten carbide swing mill for chemical analysis. The second split was crushed to <3 mm for mineralogical investigation. The mineralogical subsplit was put into a low temperature asher to generate low temperature ash (LTA) for XRD mineral identification and for SEM-EDXA, microprobe examinations.

### 2.2.2 Low Temperature Ashing

In order to determine coal mineralogy, approximately 100 selected coal samples were ashed using a LFE LTA 302 low temperature ashing machine, following similar operating conditions to those described by Newman (1988). The temperature in the

ashing chamber was around 170°C. The resultant LTA samples were ground and made into powder slides which were then subject to X-ray diffractometry (XRD) determination.

### 2.2.3 Float-Sink Separation Test

Heavy liquids have been commonly used to separate the minerals of different densities. In this study, a number of attempts were made to separate mineral-matter-rich sink fractions and organic-matter-rich float fractions on four sets of E seam-composite coal samples using heavy liquids. The liquids used in the separation were perchlorethylene [Specific Gravity (Sp.G.) = 1.71 g/cm$^3$] and petroleum spirit (Sp.G = 0.72 g/cm$^3$) mixtures. The desirable Sp.G. of heavy liquid can be achieved by simply mixing different proportion of the above two heavy liquids. The particle sizes of feed coal are 1 mm and <60 μm. A centrifuge (at speed of 2000 rpm to 4000 rpm) was also used in several separation trials. After each separation, sink and float fractions were filtered and dried in an oven overnight at a temperature of 40°C.

### 2.2.4 Coal Sequential Leaching

In an attempt to quantify the modes of occurrence of elements in coal, a sequential leaching test was performed on three seam-composite samples of E seam coal. The leaching procedures used in this study are similar to that described by Palmer et al. (1993).

Duplicate 5 g coal samples, with particle size of < 250 μm, were weighed into 50 ml polypropylene tubes. Each tube was sequentially leached with 35 ml each of 1N ammonium acetate ($CH_3COONH_4$), 2N hydrochloric acid (HCl), concentrated hydrofluoric acid (48 wt% HF) and 2N nitric acid ($HNO_3$). During each of the above leaching stages, each tube was held by finger-clamp and shaken for 18 hours using a motorised shaker. Gases may form during the leaching procedures due to decomposition of carbonates, sulphides and other minerals. In order to allow gas escape but prevent release of liquid, each tube was enclosed in a polyethylene bag tied by a plastic coated

wire strap. Each of the above bags was then enclosed in a second polyethylene bag tied by a plastic coated wire strap.

The leaching sequence described above was adopted so that ideally and theoretically (1) the first step $CH_3COONH_4$ would remove all the exchangeable cations, (2) then HCl would remove cations associated with carbonates and monosulphides, likewise (3) HF would remove cations associated with silicates, and finally (4) cations associated with disulphides (pyrite) would be removed by $HNO_3$. Unleached components may be associated with organic matrix or "shielded" mineral grains encapsulated by the coal matrix.

A representative split of the original unleached coals was analysed by instrumental neutron activation analysis (INAA), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and cold vapour atomic absorption (CVAA). After each leaching step, approximately 0.5 g of residual solid was taken for INAA and for Hg analysis by CVAA. The resultant leachates at each leaching step were also saved for the analysis of ICP-AES and ICP-MS.

Although this sequential leaching test has the capability of determine whether a trace element is associated with a specific leachant (AmAc, HCl, HF and $HNO_3$), it has its own limitations of determining exact phases a trace element may associated with. For example, trace elements in HCl leachate indicate an association with HCl soluble phases (carbonates and/or phosphates). The sequential leaching tests itself cannot distinguish whether the trace element is associated with carbonates or phosphates or both. Nonetheless, it is a very useful tool for determine the trace element association, especially when combining with the results from other techniques.

## 2.3 Analytical Methods

In order to determine trace element concentrations and the spatial distribution of trace elements in the Greymouth coals as well as in their combustion products, several analytical facilities were employed in this study.

### 2.3.1 X-ray fluorescence (XRF) analysis

A Philips PW-2400 wave-length dispersive X-ray fluorescence (WD-XRF) spectrometer in the Department of Geological Sciences, University of Canterbury, was used to analyse bulk rock samples for both the major elements and selected trace elements. In this study, XRF has been used routinely to analyse major elements (Si, Al, Ti, Fe, Ca, Mg, Mn, K, Na, P, S) of both high temperature ash (HTA) of coal and sedimentary rocks. Samples are prepared as fused glass discs following a procedure similar to Norris and Hutton (1969) and Leake et al. (1969). The lower limits of detection (LLD) are listed in **Table 2.1**.

In addition, wave-length dispersive X-ray fluorescence was also used to analyse selected trace elements V, Cr, Ni, Zn, Zr, Nb, Ba, La, Ce, Ga, Pb, Rb, Sr, Th, Y, F, S, Cl, As and Se on whole coal powder samples as well as sedimentary rocks (roof and floor rocks, inorganic parting rocks). Samples were prepared as compressed powder pellets following similar procedures to Norris and Hutton (1969) and Leake et al. (1969). The LLD for selected trace elements are given in **Table 2.1**. Some international whole-coal reference materials from the U.S National Institute of Standards and Technology (NIST) 1632b, 1633b, 1635, and from South Africa Reference Materials (SARM) SARM-18, SARM-19, SARM-20 were used to calibrate trace element concentrations. The certified values for the trace elements in these seven international coal reference samples are given in **Appendix 2**.

Of the 184 samples collected, 141 were analysed for major elements using WD-XRF. All 184 samples were also analysed for trace elements using WD-XRF. The random analytical error (precision) for major and trace elements for WD-XRF are given in **Table 2.2** as a measure of the precision of this method.

### 2.3.2 X-ray diffraction (XRD)

In order to determine what minerals occur in the Greymouth coals, powder slides of LTA, inter-seam inorganic parting, roof and floor sedimentary rocks were prepared and performed on Philips PW 1720 X-ray diffractometer in the Department of Geological Sciences, University of Canterbury.

### 2.3.3 Scanning Electron Microscope Equipped with Energy Dispersive X-ray Analyser (SEM-EDX)

Scanning electron microscopes (SEM) are primarily designed to observe and record high-resolution secondary and backscattered images from any solid samples, which are normally three dimensional and not polished. However, energy-dispersive x-ray spectrometers (EDX) are often fitted into SEM to allow rapid qualitative or semi-quantitative analysis of samples for mineral identification. In this study, a Leica-S440 SEM with Oxford Instruments EDS detector plus Robinson backscatter detector in the University of Canterbury was employed to scan and analyse many polish block samples as well as mineral grains mounted onto glued stubs for mineralogical study. Detection limits (DL) are 0.2% to 0.7 wt% for major element oxides and 1% for most trace elements (Potts, 1987).

### 2.3.4 Electron Microprobe (EMP)

Microprobe analysis involves the excitation and chemical analysis of selected areas of diameter as small as a few microns on the surface of samples. Therefore, specimens must be prepared as polished thin sections on a glass slide or as samples polished in a resin block. Microprobe analysis is especially useful to determine the individual mineral grains in thin section or in polished block samples. In this study, a JEOL JXA-8600 Superprobe was employed to analyse individual minerals (crocoite, pyrite and clay) in Department of Geology, University of Otago. The LLD for microprobe analysis are usually +/- 0.07 to

0.42 wt% for major elements and 0.04 to 0.39 wt% for selected trace elements obtained in this study.

### 2.3.5 Instrumental Neutron Activation Analysis (INAA)

Because the concentration of many trace elements fall below the detection limits of XRF, 95 out of 184 samples were also analysed using INAA. INAA is one of the most powerful and unique analysis techniques for selected trace elements. This technique is used predominantly for analysing specific trace elements down to detection limits in the ppm to ppb range, and is especially sensitive for the rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu), Sc, Co, Cr, Cs, Hf, Ta, Th, U and some others. INAA involves the irradiation and analysis of rock powder or grains that undergo no chemical treatment (non-destructive) in the course of analysis. INAA has the advantage of being (1) very sensitive for specified elements, (2) free of matrix interference effects (except overlap interferences in complex gamma spectra), and (3) no chemical treatment needed for sample preparation. However, INAA has the disadvantage of requiring specialised irradiation facilities and for this reason is largely confined to establishments adjacent to nuclear reactors. In this study, INAA was used to analysis more than 30 trace elements on whole coal, low temperature ash (LTA) and mineral samples as well as sedimentary rock samples. Seven international whole-coal reference materials, such as NIST 1632b, 1633b, 1635 from the U.S National Institute of Standards and Technology (NIST), and SARM-18, SARM-19, SARM-20 from South Africa, as well as CLB-1 from U.S Geological Survey were used to calculate pure trace element intensities.

As a measurement of the precision, the comparison of certified concentrations to the measured concentrations of trace elements as well as standard deviations in the INAA analysis are given in **Table 2.3**. The plots of certified concentrations against averaged measured values show an excellent agreement for all trace elements except Hg and Zn. All those plots (**Appendix 3**) show linear correlations except Hg and Zn. The disagreement of Hg with reported values is clearly caused by unresolved analytical difficulties, so Hg value should be considered as estimates only. The discrepancy of Zn is

with the South Africa Reference Materals (SARM) standards which are systematically lower. It is believed that the SARM values are in error. INAA analyses were performed by Professor Nelson Eby at the Department of Environmental, Earth and Atmospheric Sciences, University of Massachusetts, Lowell, USA.

### 2.3.6 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to analyse 35 major and trace elements on the leachate samples derived from the coal leaching tests in this study. The outstanding advantage of ICP-AES is the possibility of analysing 20 to 60 elements simultaneously in a cycle time of 2-3 minutes on a modern instrument fitted with a direct reader polychromator. However, the drawback of ICP-AES, especially for the determination of trace elements, is the spectrum overlap interferences. The detection limits for most trace elements are <0.1 μg/ml for the ideal solution (**Table 2.1**). ICP-AES analyses were performed in the U.S. Geological Survey in Lakewood of Colorado, USA.

### 2.3.7 Inductively Coupled Plasma-Mass Spectrometry ICP-MS

The two most important advantages of ICP-MS are the inherently low background intensities and freedom from matrix interferences observed in mass spectra. ICP-MS can determine simultaneously a wide range of trace elements, often down to 0.1 to 2 ppb (**Table 2.1**), using a simple sample dissolution without pre-concentration treatment. In this study, ICP-MS was used to determine 22 trace elements for the leachate and solid residue samples resulted from coal leaching tests. The detection limits of ICP-MS for application of multi-element silicate rock analysis are, in general, significantly lower than for ICP-AES. ICP-MS analyses were performed in U.S. Geological Survey in Lakewood of Colorado, USA.

### 2.3.8 Petrography

In addition to the analyses list above, a Zeiss UMSP50 optical microscope with photometry, UV and spectral scanning capabilities was also employed for qualitative petrographic characteristics of selected polished coal samples. Optical microscopy was undertaken in both white and fluorescent lighting modes. Sample preparation for petrography has been previously described by Li et al. (1999b, 2001a).

### 2.3.9 Proximate and Ultimate Analysis

In order to determine the coal rank and coal quality, proximate analyses (moisture, ash, volatile matter, fixed carbon and sulphur content) were also employed in this study. The proximate analysis results for selected Main seam samples are given in **Appendix 4**. The proximate analysis was carried out in CRL Energy Ltd, Lower Hutt, followed the standard methods given in **Table 2.4**. Ultimate analysis was carried out by Geochemical Testing of Energy Centre, Inc. in USA following ASTM (1992) standard methods given in **Table 2.5**.

In addition, forms of sulphur were also analysed by following the standard method of D2492 in Geochemical Testing of Energy Centre, Inc., Pennsylvania, USA.

# Chapter 3

# Chapter 3 Mineralogy and Geochemistry

## 3.1 Introduction

Previous investigations of the Greymouth Coalfield have been conducted by Gage (1952), Laird (1972), Nathan (1978), Thorburn (1981), Bowman (1982), Newman (1985), Sherwood et al. (1992), Moore (1996b), and Ward (1997), among others. However, The focus of most of these studies has been on either stratigraphy, sedimentology, depositional settings or palynology. Soong and Gluskoter (1977) did a study on the mineralogical composition of 13 New Zealand coal ashes, but only one sample (from the Strongman No. 1 Mine) was in the proximity of the area covered by the current project. Newman (1988) carried a detailed investigation of mineral matter, but the emphasis was on the Eocene age Brunner Coal Measures, rather than the Cretaceous coals. In fact, no systematic study has been undertaken on either the Main or E seams to investigate their low ash and inorganic characteristics. Although there are many coal seams within the Greymouth coalfield, this study has chosen to focus only on the Main and E seams of the Rewanui Coal Measures (for geographic locations, see **Fig. 1.5**). This chapter will accomplish the following objectives: (1) examine the low-ash nature of the two coal seams, (2) determine the mineralogy and geochemistry, and finally (3) propose and discuss the leaching mechanisms which may be responsible for the low inorganic content of these coal seams.

## 3.2 Low Ash Nature of the Coal

The two most interesting features of the Greymouth coal seams are their thickness (up to 35 m) and low ash content (<0.6% in some cases). The coals are laterally discontinuous, as a result of both faulting and rapid sedimentary facies changes. Drilling and coal resource exploration programs undertaken by government and private companies in the last 30 years have generated numerous geological and coal quality data. In order to understand the relationship of seam geometry and spatial distribution of ash yield and sulphur content, all the available quality data (R. Boyd, pers. comm., 2000) were

compared with stratigraphic, geophysical and lithological data (J. McNee, pers. comm., 2000). Using these data, isopach maps for thickness, ash yield and sulphur content were constructed for both the Main and E seams. The thickness for the two seams and the ash variability in the Main seam is shown in **Figures 3.1 to 3.3**.

The thickness of the Main seam ranges from 1 to 35 m (but is typically 10 to 20 m) (**Fig. 3.1**). The thickest part of the Main seam trends approximately north-south, and it thins both to the east and west. Coal thickness decreases are a result of lateral facies changes where the coal inter-fingers (i.e. "coal splitting") with inorganic sediments (Moore, 1996b). There are few places worldwide where Cretaceous age coals attain these sorts of thicknesses.

The E seam, which is stratigraphically higher (approximately 20-50 m), shows a slightly different geometry (**Fig. 3.2**) and is generally thinner than the Main seam. The thickest part (up to 14 m) of the E seam is present only in the northern part of the basin. Towards the south of the basin, where the Main seam is located, the E seam becomes thinner and is usually less than 4 m thick.

What also makes the Cretaceous Greymouth coal seams anomalous are their extremely low ash yields. In the 109 ply coal samples (excluding roof and floor sediment samples) analysed in this study, both the E and Main seams generally have ash yields of < 3% (air dry basis – adb, **Table 3.1**). **Figure 3.4** shows distribution histograms for ash yield for the 109 samples. Among those samples, 16 samples (or 15% of total samples) have ash yields of 0.57% to 1%, 76 samples (or 70%) have ash yield of <3%; 90 samples (or 82% population) have ash yields of <5%; in contrast, only 19 samples (or 18% of sample population) have >5% ash yield and most of them are in contact with either roof, floor or inorganic parting sediments. These higher ash intervals sometimes approach ash yields of 24% or higher. In another broader survey of ash yields in 94 Main seam-composite samples from the drilling log database (R. Boyd, pers. comm., 2000), it was found that 58 (or 62% of total populations) samples have ash content of <6%. Therefore, Greymouth coals even in seam composites have very low ash contents. In contrast, other Cretaceous

coals worldwide have ash yields (on dry whole seam basis) ranging from 10% to 25% (McCabe & Parrish, 1992). In fact, most coals, irrespective of age, have ash yields at least 5% to 10%. So why are the Greymouth coals so low in ash? To answer this question, the mineralogy and geochemistry has been examined to enable models to be developed.

Not unsurprisingly, the lowest ash yields for the Main seam are well correlated with the thickest parts of the seam (**Figs. 3.1** and **3.3**). Towards all margins, ash yield tend to increase, especially towards the east and northwest margins. The two highest ash zones (shown in **Fig. 3.3**) located in the northwest and eastern parts of the study area are probably related to the original detrital inorganic sources of the Greymouth coals. Bowman (1984) divided the Rewanui Coal Measures broadly into two distinctive zones in terms of the provenance of the sediment: (1) in the north west and western parts of the basin the sediments are characterised by high-energy-transported bedded greywacke conglomerate, and upward fining cycles with sandstone, mudstone and coal, which are thought to be derived from the Greenland Group greywackes and argillites. In contrast (2) in the east and southern parts of the basin the sediments are characterised by quartzofeldspathic sandstone and upward fining cycles with mudstone and coal, which are thought to be derived from a granitic source which probably came from at least 20 km north of the present position of the coalfield. Therefore, the northwestern parts of the basin were prone to being inundated by a clastic detritus derived from the erosion of the Greenland Group rock. The higher ash zones along the east margins (**Fig. 3.3**) are thought to be related to fluvial palaeochannels, which periodically flooded the peat margins and supplied granitic-derived sediments (Bowman, 1982, 1984; Newman and Newman, 1992).

In order to further understand ash-yield spatial distribution, six vertical seam profiles for the E seam and four vertical profiles for the Main seam were investigated in detail. **Figure 3.5** shows ash vertical variations in both the E and Main seams. Nine out of 10 ash yield profiles demonstrate that ash yield is generally around 3% across most part of the seam except at the bottom and/or top layers, which are in contact with roof, floor or

inorganic parting sediments, where higher ash yields (up to 60%) may be present. For example, in the ash profile DH 703 with a coal thickness of 21m (**Fig. 3.6**), the ash yields are around 2 to 3% (adb) at both the top and the bottom of the seam. However, the ash yield decreases dramatically toward the centre where it is as low as 0.58%. The ash profile of DH 755 is very similar to that of DH 703, perhaps because these two sampled locations are only approximately 200 m away and were affected by the same depositional environments (**Fig. 3.6**). The ash content increase from point A to point B (**Fig. 3.6**) in the profile DH 703 is probably correlated to the inorganic parting of DH 755 due to the same flooding event as seen in DH 755 (**Fig. 3.6**). Moore (1996b) had also correlated this interval as well based on lithotype. Nine out of 10 seam profiles investigated followed a similar distribution pattern; in contrast, location O/C2 (**Fig. 3.5 box c**) demonstrates the opposite vertical variation pattern.

In addition, another interesting aspect is that the ash-yields in the Greymouth coals are lower than what is found in most peats worldwide (**Table 3.2**). Even low ash peat has ash yields generally in the range of 1% to 5% (Ruppert et al., 1993; Moore et al., 1999; Moore and Shearer, in press).

## 3.3 Coal Mineralogy

The inorganic components in coal occur either as discrete mineral grains or are bound organically. The chemical elements in coal are mostly associated with the mineral phases in the form of aluminosilicates, carbonates, sulphates (Gluskoter, 1977; Swaine, 1990), sulphides and oxides.

Mineral phases can be identified by using XRD and even be quantified from X-ray diffraction study of whole-coal samples using a Rietveld-based interpretation method (Mandile and Hutton, 1995; Hutton and Mandile, 1996; Ward et al., 1999). Ash mineralogy was investigated using XRD, SEM-EDXA and microprobe analysis on approximately 100 LTA samples collected from both the E and Main seams. The coal mineralogy is summarised in **Table 3.3**. Ash consists mostly of clays (mainly kaolinite

and illite with minor amounts of smectite) and quartz in both seams. In addition, the Main seam commonly contains minor amounts of sulphides (mainly pyrite) but with only trace amounts of carbonate. In contrast, the E seam commonly contains carbonates (siderite, calcite, ankerite) and phosphates (apatite, crandallite) but with no, or merely a trace, amount of sulphides (mainly pyrite). Both seams also have trace amounts of sulphates, oxides, salts, and other silicates (Li et al, 1999a). The presence of crocoite was also noted by Li et al. (2001b) in both seams. As with other coal seams, it was observed that the grain size of inorganics increased as ash yields became elevated. This is especially true for quartz and clay aggregates, which compose the bulk of the ash.

The mineral compositions can be calculated using major element analysis data of coal samples. The major element data came from this study and the drillhole coal quality database of former Greymouth Coal Operating Limited[2], Spring Creek mine license (hereafter called GCOL database) (R. Boyd, pers. comm., 2000). Using 89 sets of major element and sulphur analyses (see **Appendix 5**) of seam-composite samples from 69 drill holes in the GCL database, average mineral proportions in seam-composites were calculated. The calculation was based on the following assumptions: (1) because no significant amount of K-bearing and Na-bearing minerals other than illite were found, all $K_2O$ and $Na_2O$ in ash are assigned to illite, (2) after deducting the proportional $Al_2O_3$ present in illite, the residual $Al_2O_3$ is thought to occur in kaolinite, (3) after deducting the proportional $SiO_2$ present in both illite and kaolinite, the residue $SiO_2$ was calculated as occurring in quartz, (4) all $P_2O_5$ occurs as apatite, and (5) all "pyritic sulphur" occurs as pyrite. The calculated mineral composition results are given in **Appendix 6**.

The summarised histogram results of kaolinite, illite, clays (kaolinite + illite), and quartz are given in **Figure 3.7**. The calculated results show that clay minerals including kaolinite and illite mostly vary from 40% to 70% of the total minerals in most seam-composite samples in the 69 drillholes. In contrast, quartz in ash mostly ranges from 20% to 50% of the total minerals. The calculated results generally support the mineralogical

[2] now wholly owned by Solid Energy New Zealand Ltd.

observations made using microscopy and XRD, although the observed illite proportions are lower than the calculated values possibly as a result of its poor crystallinity.

### 3.3.1 Clay Minerals

Clays, mainly kaolinite, generally comprise 50% to 70% of the total minerals present in the coal although in a few cases quartz dominates in the lower part of the coal seam (up to 50%) adjacent to inorganic partings or floor rocks. Kaolinite occurs in at least three distinctive forms which probably is related to their formation at different stages or under different diagenetic conditions. The three stages are thought to be:

(1) *Syngenetic clays*: as finely-crystalline flakes and aggregates, up to a few microns in size, intimately disseminated in organic matter. Interestingly, sometimes clay and coal can be seen as complex intergrowths. This finely-crystalline syngenetic clay is thought to have formed from mineralised solutions percolating through the coal-bearing sequence during the early stages of burial.

(2) *Epigenetic clay*: kaolinite is also present as a tabular sheet (a few cm wide), and in the form of cleat- or fracture-fillings. Another kind of kaolinite was found occurring as clusters of white fibres, possibly resulting from re-crystallization of Al-Si-bearing solution. This is interpreted as an epigenetic clay because it is thought that these types of clays form during the later stages of burial. Under SEM, kaolinite consists of hexagonal platelets and curved stacks of plates. These types of clays are distinguished from the first type by (a) having a coarse grain size of up to a few centimetres, (b) possessing a euhedral shape, and (c) containing much lower concentrations of trace elements (see Section 4.4 of Chapter 4 for more details).

(3) "*Clay conglomerates*": This kind of clay is usually associated with inertinite macerals and is mixed with sulphides, mainly pyrite, and sometimes intergrown with pyrite or carbonates. This kind of clay may result from deep weathering of detrital granite.

In those samples examined in this study, illite is only present in significant amounts (XRD detectable at >5%) in the lowest part of the Main seam and in high-ash coal samples in contact with inorganic partings. Illite was not detected under XRD in concentrations as abundant as calculated percentages based on major element analyses. There are two possibilities why illite may not be detectable: paucity of K in the coal and/or the poor crystallinity of illite. The acidity (pH) also affects the crystallisation of illite. Inter-layer clays, such as smectite, are not commonly seen but are sometimes associated with fusinite.

The crystallinity of clay minerals can vary slightly within the seam and between seams. An attempt was made to study the crystallinity of clay minerals using methods described by Murray and Lyons (1956) and Dimanche et al. (1974) by comparing the diffractogram patterns of random powder preparations. The crystallinity reflects the layer stacking order. However, the crystallinity of kaolinite in the Main seam shows only slight differences. A general trend of crystallinity was only obtained for a thick section of the Main seam in DH 703 (24m thickness). In this drillhole, the crystallinity of clay minerals (mainly kaolinite) tends to improve downward from the roof. The crystallinity of illite is closely related to $K_2O$ concentration. Clay minerals also show leaching features, such as dissolved boundaries, and sometimes the aggregates have been almost totally leached, being represented only by tiny residues (**Fig. 3.8**).

### 3.3.2 Quartz

Quartz is one of the most common minerals in both the E and Main seams, usually present as three different forms: (1) As clastic debris and individual clasts (such as sand, grit, pebbles, and rounded quartz, or part of greywacke, granitic constituents). (2) As euhedral, lenses or lensoid, subangular to semi-rounded grains, sometimes occurring as clusters parallel to seam bedding. Some quartz grains also accommodate inclusions, such as zircon. These two types of quartz were most likely brought to the swamp during peat accumulation and are of a detrital origin. (3) Quartz is also present as finely-crystalline discrete grains (less than 5 μm) intimately dispersed in the organic matter. This silica

appears to be mobile under certain conditions within the peat-forming environment. This syngenetic quartz may be the result of precipitation or crystallisation of dissolved silica solution either due to weathering of feldspars or mica, or from a mobile leaching solution. Andrejeko et al. (1983) point out that the interiors of some modern peat deposits are substantial reservoirs of amorphous silica, derived from the degradation of diatoms, sponge spicules and siliceous phytoliths associated with the organic matter.

One of the notable features of the Cretaceous Greymouth coals, especially the E seam, is the presence of rounded, often polished, pebbles up to 5-10 cm diameter, occurring as isolated clasts in the coal seam. These pebbles are termed "Chuckie stones" by the local miners. The composition of these chuckies is predominantly quartz but greywacke and granite pebbles are also commonly seen. Chuckie stones are relatively abundant and one or two are frequently intersected in most seams. They tend to be concentrated in preferred zones or horizons and are most common in coal seams associated with conglomeratic sediments (Bowman, 1982). These chuckie stones are believed to represent materials trapped in plant debris (e.g. tree roots) which is rafted into the peat swamp during flooding and becomes stranded and incorporated into the peat deposit (Bowman, 1984).

Another observation is that some quartz grains show clear dissolution features along boundaries (**Figs. 3.9a and 3.9b**). Dissolution of quartz was also observed in peats by Cohen (1972), Andrejko et al. (1983) and Ruppert et al. (1993). Furthermore, quartz, clays and carbonates (calcite mainly) are often distributed along cleats in the Greymouth coals (**Fig. 3.10**), suggesting post-burial mobilization of these minerals.

### 3.3.3 Carbonates

Carbonates, mainly siderite, are commonly seen in the E seam coal. Siderite usually occurs as dull-brown coloured, discrete spherical grains or nodules with sizes ranging from a few millimetres to a few centimetres. Calcite commonly occurs secondarily as in-filling cleats.

Carbonate is not as commonly seen in the Main seam as in the E seam. Most carbonates occur as infilling minerals within cleats or at maceral boundaries. They are especially prevalent in intervals in contact with inorganic partings or intervals near the floor (e.g. samples 755-T and 755-N respectively). Calcite occurs as euhedral grains, pseudomorphs, or massive (e.g. *en masse*) minerals in highly carbonaceous, high-ash intervals or associated with partings. Siderite is commonly present as round nodules associated with inertinite and occurs as discrete grains dispersed in vitrinite. Ankerite was only present in significant amounts in the thin and high-ash dull-coal interval (e.g. 755-N) close to the mudstone sediments.

### 3.3.4 Pyrite

Pyrite commonly occurs in the Main seam but not the E seam. Pyrite occurs as three different forms in the Main seam:

(1) *Syngenetic pyrite* is most likely formed during the peat stage. It is generally quite fine-grained and is disseminated throughout the organic matter. This kind of pyrite may be formed during the very earliest coalification stage (soft brown coal).

(2) *Epigenetic pyrite* has been observed as occurring locally within the Main seam, especially in the lower seam. This pyrite is within the cleat network of the coal. It usually occurs as many single discrete euhedral grains, or coalesced to form masses and sheets which coat the face of the cleats, or as infillings deposited within cleats, cracks, or fractures, from tens of microns to several centimetres in size. Some workers have termed this "massive" or "cleat" pyrite (Gluskoter, 1977; Frankie and Hower, 1987). This kind of pyrite is interpreted as epigenetic pyrite and is formed from mineralised solution after peat deposition. The pyrite is usually relatively clean, although in some cases has micro-fractures admixed with another phase or contains inclusions, commonly accompanied by clay minerals and/or quartz. Smyth (1966) noted that some primary siderite can transform into pyrite by interaction with $H_2S$-containing solutions. The formation of epigenetic pyrite is dependent primarily on the

availability of reduced S, dissolved cations (ferrous iron) and a suitable site for deposition (e.g. within cleats).

(3) *Clustered pyrite associated with inertinite* is the third kind of pyrite present in the Main seam (**Fig. 3.11**). These occur as either fusinite cell-fillings or impregnations of fusinite or semifusinite with pyrite (replacing original plant tissue from percolating solutions). This kind of pyrite is believed to be epigenetic origin.

### 3.3.5 Sulphates

Gypsum has been observed as white, opaque, cleat-filling sheets, or as veinlets in the joints usually with a shear surface in the Greymouth coals. Gypsum was also found occurring as elongated euhedral crystals in the vitrinite matrix, and possibly formed after coalification, or even later (such as during the storage), as a secondary mineral. Dehydrate occurs as a fibrous assemblage associated with vitrinite.

Ammonium-bearing tschermigite was detected in a trace amount by XRD in the LTA of some Main seam coal samples. It may be derived as a decomposition product of nitrogen compounds present in the organic matter. This is consistent with Ward (1991), who also noted this mineral in the LTA of leached Thailand coal samples, and in the LTA of leached South Australian low-rank coal samples. Ward (1991, 1992) suspected the $NH_4^+$ in Australian samples was a residue from the ammonium acetate solution, that he used for leaching his samples.

### 3.3.6 Phosphates

Apatite and monazite were also detected in both seams, especially in the E seam, under XRD and SEM-EDXA analysis in the course of this study.

Phosphates are commonly found as apatite [$Ca_5(PO_4)_3(F,OH)$] group and aluminophosphate goyazite [$SrAl_3(PO_4)_2(OH)_5H_2O$] group minerals in Australian coals (Ward, 1974, 1978; Ward et al., 1996, 1999) and US coals (Finkelman and Stanton, 1978;

Finkelam, 1980) as well as other coals. Electron microscope studies (Palmer and Wandless, 1985; Corcoran and Saxby, 1990; Ward et al., 1993) indicate that P is present as solid-solution in the group of minerals goyazite [$SrAl_3(PO_4)_2(OH)_5H_2O$], gorceixite [$(BaAl_3\ (PO_4)_2(OH)_5H_2O$], crandallite [$CaAl_3(PO_4)_2(OH)_5H_2O$] and possibly florenceite [$CeAl_3\ (PO_4)_2(OH)_5H_2O$]. Ward et al. (1996) reported that apatite and aluminophosphates most commonly occur as infillings in the pore spaces and cell cavities of inertinite macerals, and the P was mainly derived from phospho-proteins in the organic matter of the original peat deposits.

### 3.3.7 Other Trace Minerals

Crocoite ($PbCrO_4$) crystals were found in both the Main and E seams. Crocoite crystals occur as red tabular crystals with sizes ranging from < 1 mm to 2 mm (**Fig. 3.12**) in the Main seam, but frequently as brightly orange coloured, cavernous or hollow clusters (**Fig. 3.13**) in the recently exposed underground faces of E seam. Therefore, it ruled out the possibility that crocoite was only formed from the oxidation process during later storage stage. For a more detailed mineralogical description, see Section 4.5 of Chapter 4.

Rutile crystals are commonly seen in clay minerals in the Main seam, mostly as inclusions. Rutile or anatase was seen as discrete grains under SEM-EDAX. Halite and sylvite grains are sometimes found as fine grains dispersed in organic matrix in the Main seam, and may indicate a relatively low ground water level or the presence of mobile solutions leaching through the coal. In addition, muscovite and biotite were also detected under microscopy and SEM-EDX analysis; small amounts of mica are probably preserved as residues derived from the erosion of granite or granitoids.

## 3.4 Geochemistry

### 3.4.1 Major Element Variations in the Coal Seam

As previously discussed in Section 3.2, lateral distribution of ash content (**Fig. 3.3**) indicates that high ash zones are closely related to the two possible inorganic sources inferred from previous studies (Bowman, 1982, 1984; Newman, 1985).

In the study area of the Main seam, ash yield and the major elements Si, Al, K and Ti vary laterally in a very similar manner to each other (**Figs. 3.3 and 3.14** to **3.17**). This is exactly what it is expected because Si, Al and K (as clays and quartz) are the controlling factors in the ash yield as a result of clays and quartz being the dominant minerals in the coal. In addition, Ti is also primarily associated with clay minerals as discrete oxide (rutile or anatase) inclusions in clays.

The lateral variation trends of Si, Al, K, Ti and ash yield are probably related to controls on the original detrital clastic sources of the Greymouth coal basin. Rare earth element signature also supports this and is further discussed in Section 4.6.3 of Chapter 4. Moreover, the two high ash content zones in the NW and SE of the study area (**Fig. 3.3**) are coincidently correlated to the two inorganic sources proposed in previous studies (Bowman, 1984; Newman and Newman, 1992). These are the Greenland Group greywacke and argillite rocks derived clastic from the NW of the basin as well as the granite and granitoids derived sediments from the eastern margin of the basin.

In the Main seam, vertical distribution of ash content is that ash contents tend to be systematically high in the lowermost bench (in some case in the uppermost bench as well) and the lowest ash contents are always in the middle bench. One exception is the profile O/C2 where the highest ash content is in the middle and lowermost benches (see **Fig. 3.5**). Major elements Si, Al, K and Ti also vary vertically concordantly with ash yield. A profile of major elements observed in DH 703 is shown in **Figure 3.18**. $SiO_2$ and $Al_2O_3$ follow the same vertical variation trend as ash yield. These trends are consistent

with the mineralogical observations that show predominance of clays and quartz in both the Main and E seams. $Fe_2O_3$ and S show a similar trend across the profile but this trend is different from that of the ash yield and $SiO_2$. Similar variations in major elements were also observed in other profiles from both the Main and E seams.

In the Greymouth coal seams, the K contents are elevated more in the basal layers than in the top portions of the seams in all locations investigated. This is interesting because potassium is one of the essential nutrients for plant growth and usually expected to be enriched in the top layers of peat due to plant bioaccumulation mechanisms.

$Na_2O$ concentrations do not show any systematic trend within the coal seam. Na was detected under SEM-EDXA as submicron discrete salt (NaCl) grains, but NaCl apparently could not account for a significant proportion of the total Na in the coal.

The Greymouth coals have low S (<1%). Among 88 seam-composite samples from the Main seam coal quality database of Solid Energy Ltd. (R. Boyd, pers. comm., 2000), 63 samples (72% of total population) have total S of <0.4% (**Fig. 3.19 box A**). S in the Greymouth coals is primarily organic S with minor amounts of pyritic S and sulphate S. The proportions of different forms of S for the Main seam are given in **Figure 3.19 box B to box D**.

### 3.4.2 Correlations with Ash Contents and Inter-element Correlations

Si, Al, K and Ti have a linear correlation (r = 0.95 to 0.98) with the ash yield (**Fig. 3.20**). Al, K and Ti also have linear correlation (r = 0.95 to 0.96) with Si in both the E and Main seams (**Fig. 3.21**). These excellent correlations confirm, from a geochemistry perspective, that clay minerals and quartz are the controlling factors on ash composition and concentrations.

The correlation between $Fe_2O_3$ and S display two obvious trends (**Fig. 3.21**), (1) a flat straight line intersects the Y axis at about 0.3% regardless of the $Fe_2O_3$ content. This trend probably reflects the organic S in the coal, (2) total S increases with $Fe_2O_3$ but again intersects the Y axis at about 0.3% (this is the general organic S in the coal), and this probably reflects the pyritic S on top of the organic S in the Main seam coal. Ward et al. (1999) reported a similar observation in the New South Wales coals of Australia.

Although $Fe_2O_3$ correlates well with S in the Main seam, it does not correlate with total S in the E seam. This may be the result of: (1) most S is organic, (2) siderite is common, and (3) pyrite is rare in the E seam.

Another interesting observation is that CaO is well correlated (r = 0.9) with the $SO_3$ in the Main seam coal (calculated from $SO_3$ in the coal ash). This probably indicates a sulphate (gypsum) occurrence.

P and Ca show a positive and an almost linear correlation to each other (**Fig. 3.21**) due to a significant phosphate occurrence for these two elements. In the sequential leaching tests of the E seam coal, 55% to 75% P and 45% to 85% Ca were HCl soluble. Apatite was observed under SEM-EDX. Therefore, phosphate (apatite) is a significant mode of occurrence for P and Ca although P and Ca are also presented in other minerals (such as REE-bearing phosphate crandallite, calcite, gypsum) in the coal.

Measured P in the Main seam coal is well correlated (r = 0.94) with $P_2O_5$ (calculated from coal ash chemistry), indicating most P has been retained in the ash after 750 °C ashing process.

P was found occurring in the apatite [$Ca_5(PO_4)_3(F,OH)$] group and aluminophosphate minerals of the goyazite [$SrAl_3(PO_4)_2(OH)_5H_2O$] group minerals in Australian (Ward, 1974, 1978) and US coals (Finkelman and Stanton, 1978; Finkelam, 1980).

In sequential leaching tests (see Section 2.2.4 for details) of the E seam coal (**Table 3.4**), 5% to 55% Ca, 0% to 15% Mg and 5% to10% Na were ammonia acetate soluble, suggesting part of Ca, Mg and Na are presented as weakly-bound exchangeable cations in the coal, presumably through carboxylic acid and phenolic or hydroxyl groups. This kind of elemental occurrence reflects the possible mobilisition of these elements, that is further discussed in Section 3.6.

## 3.5 Organic Petrographic Characteristics and Their Implications

Organic petrographic characteristics were examined qualitatively using a Ziess reflected-light microscopy. Both white and fluorescence light microscopy were employed in order to help determine organic composition of the Greymouth coals. The coals are predominantly vitrinite (85% to 95%, mineral matter free basis), with some liptinite (1-5%), and low inertinite (2% to 10%) (see also Newman, 1987a). Plant structures in vitrinite were easily recognised. Most of the liptinite is composed of sporinite, plus minor cutinite, and traces of alginite. Other characteristics are: (a) the presence of void-filling liptinitic material (exsudatinite or bitumen?) which fluoresces, (b) low inertinite content, and (c) the etched features of mineral (mainly quartz and clays) boundaries. Interestingly, the void-filling liptinitic materials infill cavities (such as cell lumens) and microcleats which connect to other larger cleats and/or fracture networks (**Fig. 3.22**), or adjacent to major cleats/fractures and mineral matter rich layers. Minerals (carbonates, pyrite, and clays) filling voids and/or replacing part of the semi-fusinite were also observed.

## 3.6 Discussion

The E seam, and especially the Main seam, have extremely low ash, with 70% of the 109 samples analysed having ash yield of 0.58% to 3%; these values are lower than those reported for most peat deposits (e.g. Shotyk et al., 1990; Neuzil et al., 1993; Moore and Shearer, in press; among others). This observation presents a central conundrum on the placement and fate of inorganic materials in these coals.

Most coal seams with ash yields less than 5% are interpreted to have been formed as raised bogs which were isolated from sediment influx. These mires were shielded from inorganics not only from their raised nature, but also through sediment baffling and flocculation of clays at the mire margins (Staub and Cohen, 1978; Cohen et al., 1987; Ruppert et al., 1993; Staub and Esterle, 1994; Cohen and Stack, 1996). The only source of moisture is thought to have been precipitation from abundant rainfall (Staub and Esterle, 1994; Cohen and Stack, 1996; Moore et al., 1999). Even invoking a raised bog scenario for the formation of the Greymouth coals cannot explain their extremely low-ash contents. Present day raised bogs that are thought to be the analogues to the lowest ash coals contain no less than 1 to 2% inorganic materials (Shotyk et al., 1992; Ruppert et al., 1993; Morre and Shearer, in press).

In order to preserve such anomalous ash yields in thick coal seams, two hypotheses are proposed. The first hypotheses is that there has been a uniquely low concentration of inorganic matter deposited during the peat stage. A quite unusual depositional setting and processes would have been required to facilitate such low concentrations of inorganic materials even if the mire was raised. Moreover, even the peat-forming plants must have been unusually low in inorganics. In a second hypothesis, inorganic matter has been removed through leaching processes both during peat formation and after burial. The purpose of this chapter is to discuss these two hypotheses and provide an explanation for the anomalously low-ash nature of the Greymouth coals; furthermore, the mechanisms discussed here may provide an answer and insight into explaining other low ash coals such as Brunner coals in Westland of New Zealand, Blue Gem coals in Eastern Kentucky, and lignites in southern Victoria of Australia and Indonesia, among other deposits.

Both the Main and E seams were deposited in a fault-controlled rifting basin, associated with alternating fluvial and lacustrine sediments in a fresh water environment (Newman and Newman, 1992). The tectonic complexity and differential subsidence caused both seams to be laterally discontinuous, with individual pods roughly 3x3 km in size. The low sulphur content (**Table 3.1**) and the absence of marine-related minerals support previous

interpretations that the coals were formed in a fresh water environment (Gage, 1952; Bowman, 1982). Other Cretaceous coals with similar depositional and tectonic settings (Fielding, 1992; Langenberg et al., 1992; Holfman et al., 1992) are found to have, on average, ash yields of greater than 10% (**Table 3.2**). Furthermore, even in the thick centre portions of Cretaceous coals, as a rule, ash yields do not approach the low values observed in the Greymouth coal seams.

A palynological study of the Main seam by Moore (1996a) concluded that the coal was formed from a gymnosperm-dominated vegetation community. Most samples examined in the study contained <10% angiosperms, with most of the variations occurring in the gymnosperm and spore types (e.g. *Phyllocladidites mawsonii* 30-70%; *Gleichenia* spores only exceed 10% at the upper part of Main seam). Although other gymnosperm-dominated coals exist elsewhere e.g., those coals (Rich et al., 1988; Roehler, 1982; Crowley et al., 1994; Warnes, 1990; Saward, 1992; Shearer and Moore, 1994) generally contain ash yields significantly higher, although in some cases as low as the Greymouth coals.

Overall, the palynological evidence does not distinguish the Greymouth coal seams from other Cretaceous coals worldwide. The Main and E seams probably formed as raised peat deposits. This in itself would inhibit introduction of detrital sediments into the seam (McCabe and Parrish, 1992). However, as pointed out previously, many other coals interpreted to have formed as raised or domed peat deposits have higher ash yields than those observed in the Greymouth seams. Even more perplexing, peats which are currently forming in Indonesia, New Zealand, Malaysia, among other places, have ash yields greater than 1 or 2% (**Table 3.2**). If all of the mineral matter were to remain in these raised peat deposits, this would result in ash contents in the coal significantly higher than 1-2%. It appears from the evidence of the Main and E seam deposition setting and plant types, as compared to these same parameters in other coal seams, that they cannot account for such low-ash contents.

However, optical microscopy gives a few clues to why mineral matter in the Greymouth coals is so low. Void-filling liptinitic material (exsudatinite and/or bitumen) is considered to be produced during the late diagenetic stage (Teichmuller, 1974; Mastalerz and Glikson, 2000). Cohen and Bailey (1997) also reported void-filling liptinitic materials in artificial coalification experiments. Recently, solid bitumen in coals has also been suggested to be an important source of gas in Bowen Basin coals over a wide range of maturation levels (Glikson et al., 1999). After heating lignite, Glikson (pers. comm., 2000) found oil and bitumen similarly present in the cleats. So the presence of void-filling liptinitic material in the Greymouth coals (**Fig. 3.22**) is a good indicator that liquid hydrocarbons migrated through the cleats or fractures in the coal seams. Shearer and Moore (1996) also found that artificial coalification of peat resulted in migration of fluids.

The association of void-filling and cleat-filling liptinitic materials with minerals in the Greymouth coal seams suggests that mineral-bearing fluids could have accompanied liquid hydrocarbons generated by the coal and migrated through the coal seam. Therefore, it is believed that, some inorganic materials were removed during this phase (in addition to the removal of inorganics during the peat and lignite stages), thus helping to lower the overall ash yield of the Greymouth coal seams.

It is also known that vitrinite and inertinite are principally derived from the same source material (such as wood, leaf, root tissue, etc.), except that inertinite is formed when these tissues are oxidised, either biochemically or by fire. The low concentration of inertinite and the extremely high vitrinite content may suggest that the Greymouth coal seams were developed in a wet climate with high water tables during the peatification process. This situation would favour the percolation of mineralised (chemical) solutions or ground water through the coal-forming sequence during its formation. The waters, including the porewater and ground water surrounding the coal seam after burial, were acidic and reducing. All of these anaerobic conditions would have retarded bacterial activities. Therefore, the seams were formed and developed under relatively reduced conditions and

were not exposed to oxidising conditions for most of the time following peat accumulation.

Another compelling evidence is that minerals in the coal were commonly observed to have been etched (**Figs. 3.8, 3.9a and 3.9b**). In some cases, whole clay aggregates have been dissolved and removed possibly by percolating solutions. Calcium carbonates, silica and clays filling cleats were also observed and are further indication that inorganics were mobile after burial.

It is postulated that the Main and E seams did contain detrital inorganics. Similarity in the chondrite normalised REE patterns of basement rocks and coal and ash samples from both the E and Main seam (see **Section 4.6.3** of Chapter 4 for more details) suggest that, at least, some of the original inorganics within the coals were of a detrital basement origin. No doubt that this detrital material would have further increased ash yield levels above what seems to be a minimum of 1 to 2% that is found in most raised peats. Therefore, to have coals with such a low ash content (0.58-2.5%), some physical and/or chemical processes to reduce the ash content must have been operating at some stage during burial and diagenesis.

Based on the data collected from the Greymouth coal seams and taking into account the published data, a model was proposed that three major stages contributed to the low inorganic matter content in the Greymouth coal (**Fig. 3.23**). At this point, it is not known which of these three stages played the most important role.

### 3.6.1 Stage 1 - Peat Accumulation.

At a temperature of < 30°C and pH of 3 to 5, decaying plants generate abundant organic acids. Those organic acids in return favour and promote the degradation and alteration of some minerals (such as quartz and feldspar). It is widely accepted that organic-acid-aided degradation and decomposition of inorganic matter in peat is very common, no matter what the peat type (domed, planar peat or a complex of both). Numerous studies on

modern peat sequences (both domed and planar) worldwide report that there is strong evidence to suggest that some minerals and inorganic ions, once deposited in the peat, can either be leached (Kosters and Bailey, 1986; Cohen et al., 1987; Cohen et al., 1990; Wills et al., 1991; Bailey and Cohen, 1993; Ruppert et al., 1993; Bailey et al., 1995), altered by organic acids (Staub and Cohen, 1978; Bustin and Lowe, 1987), or altered by in situ microorganisms (Andrejko et al., 1982). This leaching process would be especially important in the domed (ombrotrophic) portions of peat deposits or in the central portions of thick planar deposits (Cohen et al., 1987). Andrejko et al. (1983) and Cohen et al. (1987) believe that highly pitted or corroded biogenic siliceous mineral matter (as bored-sponge, spicules, corroded silicified bulliform cells) in Okefenokee peat of Georgia, is probably the result of authigenic silica dissolution from the metabolic activities of microorganisms, such as bacteria, endolithic fungi, or diatoms. Cohen et al. (1987) also suspected that some mineral matter was leached away before forming the low-ash Changuinola peat deposit in northwest Panama. Newman (1987b) also attributed the high-alumina ash West Coast coals of New Zealand to intensive and/or prolonged leaching of stable peat swamps which had a raised, rain-fed surface zone. It is likely that the Greymouth coal seams may have formed in a similar geochemical conditions to what has been described for modern peats. Therefore, concentrations of organic acids (e.g., acetic, oxalic, formic) would have been high due to thick peat accumulation and prolonged decomposition of plant materials.

Organic acids favour and promote mineral decomposition and metal complexation (Drever and Vance, 1994; Bennet and Casey, 1994). Both plant decay and organic-acid-aided mineral decomposition generate exchangeable ions (e.g., K, Mg, Na, Al). For example, Ruppert et al. (1993) reported > 90% ash-forming inorganic elements present as leachable ions in the modern Indonesian peats. Therefore, at the very least, part of the inorganic matter in the Main and E seams would have been present as leachable ions (rather than mineral phases). Provided that the climate at the time was wet and water tables were high, a substantial portion of inorganic material could have been removed from the peat.

### 3.6.2 Stage 2 - Early Diagenesis

During progressive subsidence of 1-3 km (equivalent to lignite) and increasing temperatures of 30 – 70°C, early coalification processes commenced. The pH was probably low (about 4-5.5) as Kiss and King (1977) observed in South Australian lignites. Burial and compaction led to the loss of volatile matter (mainly $H_2O$ and a little $CO_2$). The remaining inorganics (e.g., K, Mg, Na, Al) derived from mineral dissolution and plant decomposition, were mostly present as exchangeable ions such as carboxylic metals. At this stage, minerals can continue to be dissolved due to rising temperature and increasing organic acid complexation activities. Some inorganics may also be driven off from organic material because of compaction and the loss of adsorption sites during lignite formation. All of these processes would have supplied more ion-exchangeable inorganics. This scenario not only has been observed in coal seams such as the Latrobe Valley lignites by Kiss and King (1977, 1979) and some US lignites by Miller and Given (1978, 1986), but also has been confirmed in the laboratory-simulated post-burial coalification experiments by Bailey et al. (2000).

In the study of the Latrobe Valley lignite in Victoria of Australia, Kiss and King (1977, 1979) reported that more than 50% of ash-forming constituents are present not in mineral phases but associated with carboxyl groups as exchangeable ions. Furthermore, mineral phases increase whereas exchangeable ions decrease towards the seam margins, although the overall ash yield remains the same (G. Holdgate pers. comm., 2000). Miller and Given (1978, 1986) also found that 20-50% of the ash-forming constituents in some U.S. lignite and subbituminous coals are present in ion-exchangeable forms.

In a laboratory simulated coalification, Bailey et al (2000) studied changes in concentrations of major inorganic ions during simulated burial of 3 different peats (*Cladium*, *Rhizophora*, and *Cyrilla* peats) equivalent to the depth of about 1.5 km. They observed that mobilisation of the major ions (Si, Al, Na, Mg) is controlled by at least three processes: (1) loss of dissolved ions in original porewater expelled during compaction, (2) loss of adsorbed cations as adsorption sites are lost during modification of organic solids, and (3) increased dissolution of inorganic phases at later stages due to

increased temperature (especially total dissolved Si) and increased complexing by organic acids and anions (especially total dissolved Al).

Consequently, for the Main and E seams, and under the above-mentioned acidic and reduced conditions, a major part of the detrital mineral component would be decomposed and enter solution, as Kiss and King (1979) and Miller and Given (1986) reported in lignites and Bailey et al. (2000) revealed in laboratory coalification. It is therefore reasonable to propose that during early coalification stages (from peat to lignite and subbituminous coal formation) and under acidic conditions, most inorganic elements would be present as exchangeable ions (rather than in mineral-bound phases). It is likely that the amount of inorganic ions dissolved would increase with rising temperature and complexing by organic acids and anions, a proposition supported by the artificial coalification experiments of Bailey et al. (2000). Furthermore, these ion-exchangeable inorganics were vulnerable and became readily leachable by pore water, ground water and/or percolating water. Other artificial coalification experiments also show that volatiles are lost from the peat to the lignite stage (Shearer and Moore, 1996; Orem et al. 1996; Cohen and Bailey, 1997; Bailey et al., 2000). All these laboratory coalification experiments lend support to a leaching mechanism for removal of inorganics from the Greymouth coal seams.

### 3.6.3 Stage 3 - Late Diagenesis

Coalification processes continually enhanced with further subsidence (3 to 5 km) and increasing temperature from 70 to 170°C, which is believed to be required for the formation of bituminous coal (Taylor et al., 1998).

Based on the fission track results for apatite concentrates, Kamp et al. (1999) concluded that the Late-Cretaceous and mid-Eocene coal-bearing succession in Greymouth coalfield indeed had experienced maximum paleotemperatures in excess of 85°C and reached a peak of 180°C. Under such conditions, even if most $CO_2$ is released at this stage, the solutions are still slightly acidic and reducing. Drever and Vance (1994) concluded that

organic acids were very effective in complexing Al and Fe, which results in the vertical translocation of these elements in the soil profile, as observed in the present study (**Fig. 3.18**). Bennet and Casey (1994) also concluded that organic acids in a low temperature aqueous system could complex metals and metalloids in solution, thereby increasing their solubility and mobility. They also pointed out that organic acids are implicated in mineral-surface interactions where they can act in ligand exchange reactions to increase the rate of mineral dissolution independent of solution concentration constraints. In the case of aluminosilicates, organic acids can complex Al, and to a lesser degree Si, in solution, thereby changing the total solubility of the minerals. At neutral pH, Al complexes are less favoured, whereas complexes of silica may be favoured. In contrast, at weakly acidic pH, silica is not affected by the presence of organic acids, whereas Al complexes (chelated by organic ligands through a dissociative ligand exchange reaction) are stable. At this high rank stage, mineral decomposition is further enhanced by rising temperature. A higher proportion of inorganics are present as exchangeable ions due to the contribution from the decomposition of minerals (feldspar, quartz and clays). Most of these exchangeable ions are also vulnerable to the acidic conditions and could easily be leached if suitable solutions were present and migrated through the coal seam. Another factor to be considered is that with increasing rank of the coal, volatile matter is lost and that large-molecule organic components breakdown into smaller molecule units. The chemical bonding between C-C and C-H also becomes stronger (O/C, H/C ratios decrease) due to the breakdown of large-molecular organic solids. This bond-enhancement process expels the weakly organic-bonded metals and compounds (which may survive in previous stages) out of the organic molecular network, making this portion of the inorganic component more freely leachable.

The sequential leaching tests of this study, showed 95% Na, 55% Mg and 55% Ca being ammonia acetate soluble (**Table 3.4**) in the subbituminous Huntly East coal of Waikato Coal Measures, strongly indicating that Na, Mg and Ca are dominantly presented as exchangeable cations in that subbituminous coal. In a study of the Taupiri and Kupakupa coal seams within Waikato Coal Measures, Newman et al. (1997) believed that most Ca, Mg, Mn, Fe and Na have an organic affinity based on their strong negative correlations

with ash contents. Furthermore, it was also found in the Greymouth bituminous coals, up to 55% total Ca, up to 15% Mg and up to 10% Na have been removed by ammonia acetate in the sequential leaching test. This result suggests that a significant proportion of Ca, Mg, and Na are still remained as exchangeable cations in this bituminous coal, even after the prolong post-burial leaching process. This is another evidence to support the proposed theory that a significant of inorganics (Ca, Mg, Na) indeed occurred as exchangeable cations in the coal seam after burial.

## 3.7 Conclusions

The depositional settings of Greymouth coal seams are not unusual compared with other Cretaceous coals from around the world. It is recognised that the tectonic complexity may have had some influence on the paleotopography and that differential subsidence may have aided in the formation of seams which were already low in ash contents. However, leaching processes are believed to be responsible for the unusually low ash content (sometimes less than 1%). Although leaching of inorganics in peat is a generally accepted process, little is known about leaching after burial. There are several lines of evidence that suggest that mineral matter may have been removed from the Greymouth coal not only in the peat stage but also after burial. For example, etching features found in quartz grains and clay aggregates indicate that some leaching processes have taken place. In addition, liptinitic material (e.g. bitumen) in the cleat networks supports that there has been some movement of solutions through the coal after burial. These solutions may have helped to remove some of the inorganics originally within the Greymouth coals. In summary, it is proposed that the leaching processes operating not only in peat stage but also during coalification stages in the Greymouth coals are:

The dominant inorganics in both peat and coal are present as exchangeable ions rather than in mineral phases, and these exchangeable ions become readily leachable, provided that water tables are high (e.g. due to a wet climate and the subsidence).

The extremely high proportion of well-preserved vitrinite and low inertinite indicates that the Greymouth coals were indeed formed and developed under wet conditions. Void-filling liptinitic materials that infill cavities (such as cell lumens), microcleats connected to other larger cleats and/or fracture networks (**Fig. 3.22**), or adjacent to major cleats, indicate organic movement during coalification stages.

The association of these void-filling liptinitic materials with mineral matter in coal suggests that mineral-bearing fluids would also have migrated with coal-generated liquid hydrocarbons, or at least taken the same pathways (cleats, microcleats) as those liptinitic materials. The cleat-filling clays and quartz and calcite are indication of mineral matter mobilisation after burial.

Etched quartz grain boundaries suggest that there has been some dissolution by fluids. Although the dissolution of quartz is commonly seen in peat, etched quartz in cleat infills may suggest it also happened in post-burial coalification.

The leaching and/or solution percolating activities indicate the inorganics could have been remobilised from the peat through to the coalification stages, and that some of them could have been completely removed from the coal seam system. Leaching and/or percolating processes are believed to be a significant factor in accounting for the extremely low ash nature of Greymouth coals.

# Chapter 4

# Chapter 4 Trace Elements in Coal

## 4.1 Introduction to the Trace Elements in Greymouth Coal

Very little is known about the trace element concentration and distribution in coals from the Greymouth region. Some element concentrations have been reported, but these were derived from a very limited number of studies (Sim and Lewin, 1975; Soong and Berrow, 1979; Purchase, 1985; Newman, 1988). Therefore, this chapter will fulfill some of the more important objectives of this study: (1) to determine the spatial distribution of trace element concentrations in the Greymouth coal basin, (2) to delineate their modes of occurrence, and (3) to discuss, in general, the potential environmental risks.

Knowledge of spatial distribution of trace elements can be used as a predictive tool to meet the different requirements of coal users. Better understanding of the modes of occurrence of trace elements can also be used to predict trace element behaviour in beneficiation (such as the feasibility and efficiency of physical coal cleaning) as well as to predict trace element behaviour in combustion and any environmental impacts.

### 4.1.1 Concentration of Trace Elements

As detailed in Chapter 3, Greymouth coals are characterised by their low ash, low sulphur contents and great thickness. Most trace element studies in New Zealand have concentrated on the Waikato and Taranaki coals (Ross, 1957; Smidt and Whitton, 1975; Sim, 1977; Mackay and Wilson, 1978; Soong and Berrow, 1979; Black, 1981; Lynskey et al., 1984; Soong, 1984; Purchase, 1985; Gainsford, 1985). **Table 4.1** gives some trace element concentrations for Greymouth coals and other major coal-producing basins in New Zealand. Compared with other New Zealand coals, Greymouth coals appear to have relatively low As, B and S but higher Se, Cs, Pb, Rb and U contents (**Table 4.1**). Trace elements for 179 samples including coal, inorganic parting, roof and floor rocks have been analysed by WD-XRF (**Appendix 7**). Ninety-five selected samples were further

analysed by INAA and those analyses are given in **Appendix 8**. **Table 4.2** gives the mean concentration of trace elements in Greymouth coals, compared with US coals of similar rank and with the "Clark value". The "crust enrichment factors (EF) (the ratio of the concentration of element in the Greymouth coals to the concentration of element in the crust composition) show that only Se, W, and S (not a trace element but a minor element in coal) are significantly enriched in coal (EF >10), and Co and Cl are only slightly enriched (EF = 1.2 and 3.1). All other analysed trace elements are depleted in coal relative to the "average crust" concentrations (**Table 4.2**). Gluskoter et al. (1977) found only a few elements (B, As, Cl, Se) concentrated in US coals compared with the "average upper crust". Compared with the mean trace elements of US coals, Greymouth coals are at the low end of concentration of US means for most trace elements (**Table 4.2**), except for W, Co, Cs, Ni, which show relative enrichment. Some elements (As, Sb, Hg, U, Br, Zn, and S) are especially depleted with concentration levels 5 to 50 times lower than the corresponding mean value of US coals.

## 4.2 Trace Element Vertical Variations

Data on the vertical and lateral variation of trace elements in the E and Main seams have been used to: (1) construct the spatial distribution of trace elements and identify any vertical and lateral trends, (2) identify and delineate any relationships between trace element variation trends and seam geometry, (3) delineate the possible sources of these trace elements and, (4) predict the trace element contents in the mining products before the actual mining takes place. With this knowledge, appropriate measures (such as selective mining, physical cleaning, etc.) can be planned ahead of time, to minimise, and even avoid, any possible undesirable environmental or technological risks associated with trace elements in coal, or to take advantage of potential beneficial by-products.

To achieve the above aims, 184 samples were collected from six profiles of the E seam and four profiles of the Main seam. The six profiles from the E seam include four underground locations (P532 and 637 from the proximity of NW margins of the E seam, 2A/B from the central area, and 283 from the south margin of the E seam) and two

opencast locations (OPC, O/C2) from the east margin of the E seam. In addition, two profiles of the Main seam from drillholes (DH 703 and DH 755) in the northern part of the study area were taken. Another two profiles of the Main seam from the southern part of the study area (DH 819 and MU) were sampled as well. Detailed sample locations are shown in **Figure 1.5**. For discussion purposes, trace elements have been categorised into three groups. The first group includes the environmentally sensitive elements, such as hazardous air pollutants (HAPs), S, Cl and F; the second group includes rare earth elements (REE), Th and Y, based on their significance regarding the source of inorganic matter, and the third group includes all the other elements which have been analysed in this study.

### 4.2.1 Hazardous Air Pollutants (HAPs), S, Cl and F

Like other coals, the Greymouth seams contain some concentration of all the environmentally sensitive trace elements in the HAPs list specified in the 1990 US Clean Air Act Amendments (U.S. Statutes at Large, 1990). The following is a discussion of the variation for each element and whether they related to each other in the study area.

**Arsenic (As):** Arsenic in the six profiles of the E seam (**Fig. 4.1**), has a concentration of < 1 ppm on a coal basis. Arsenic can reach as high as 58 ppm in chuckies[1], these are commonly found within the E seam. In four of the six profiles, the arsenic content is relatively high in the top one-third of the seam, and then tends to decrease with depth (**Fig. 4.1**). Occasionally, arsenic has relatively higher concentrations in the bottom layer. Only two (O/C2 and 283) of the six profiles displays the opposite trend with arsenic at relatively higher concentration in the middle of the seam and lower at both the top and bottom.

However, arsenic in the Main seam not only has higher concentrations (up to 21 ppm) than in the E seam but also displays a different vertical variation trend (**Fig. 4.1**). Arsenic

[1] rounded and polished pebbles, up to 5-10 cm in diameter, that often occur as isolated clasts in the coal seam.

in the Main seam varies in the range of < 1 to 21 ppm, and tends to increase with depth, at least for the upper two-thirds of the seams in the unsplit portions of the seam (**Fig. 4.1**). In the split upper and lower subseams, arsenic also appears to increase with depth except for the very bottom layer in the lower subseam. Three roof and floor rocks have arsenic <1.14 ppm, which is in line with the Main seam.

**Chlorine (Cl):** Cl in the E seam ranges from 1000 ppm to 5000 ppm, and has much higher concentrations than those found in the Main seam. Cl in the Main seam rarely exceeds 1000 ppm. There does not appear to be any systematic trend in either the E or Main seams (**Fig. 4.2**).

**Cobalt (Co):** Co in the E seam is <30 ppm, although in inorganic chuckies (quartz, 283-I1) it is much higher (676 ppm). **Figure 4.3** shows Co enrichment at both the top and bottom of the seam in four of the six profiles. In contrast, the variation trend reverses in the other two (P532 and 2A/B) of the six profiles.

In general, Co in the Main seam has a higher concentration than in the E seam, Co increases with depth in the two profiles DH 703 and DH 755 (**Fig. 4.3**).

**Chromium (Cr):** Cr in the E seam is <40 ppm except in one inorganic parting sample (OPC) that has 68 ppm Cr. In all six profiles studied, Cr follows a similar trend to Pb in both the E and Main seams. High Cr zones are at the bottom and/or top one third of the seam with low Cr at mid-seam (**Fig. 4.4**).

Cr in the Main seam ranges from a few ppm to 100 ppm. Vertically, Cr seems to have a similar variation trend to the E seam (**Fig. 4.4**).

**Fluorine (F):** Fluorine in the E seam varies from 10 to 100 ppm. F tends to be at relatively higher concentrations at the bottom and/or top of the seam relative to the mid-

seam (**Fig. 4.5**). F in the Main seam varies in the same range as in the E seam, but shows no clear variation trend.

**Mercury (Hg):** Hg in the E seam is <200 ppb (mostly <100 ppb). In five of the six profiles (**Fig. 4.6**), Hg is enriched in the top third of the seam, and then tends to decrease with depth in the lower two-thirds of the seam, with the lowest Hg present in the bottom layer. However, one of the six profiles, O/C2 (**Fig. 4.6 box c**), shows lower Hg at both the top and bottom of the seam with higher Hg at the middle of the seam. There are not enough data to identify any trend for Hg in the Main seam. Hg is <113 ppb in the roof and floor rocks of the E seam.

**Manganese (Mn):** Mn in the E seam is in the range of 5 to 282 ppm, although it reaches 445 ppm in the inorganic parting sample. Vertically, Mn tends to be in higher concentrations at the top and/or bottom in five of the six profiles. But in the other profile, P532A, Mn displays an opposite trend, with higher Mn at the mid-seam and lower Mn at both the top and bottom of the seam (**Fig. 4.7**).

Mn in the Main seam also varies in a wide range from a few ppm to almost 400 ppm (**Fig. 4.7**). Mn in the Main seam follows a similar trend as in the E seam with high Mn content at the top or bottom of the seam.

**Nickel (Ni):** Ni in the E seam is <50 ppm. In all six profiles, Ni shows a clear mid-seam minimum concentration (**Fig. 4.8**). Likewise, Ni in the Main seam is <80 ppm, and follows a very similar trend to the E seam, with high Ni content at the top and bottom (**Fig. 4.8**).

**Lead (Pb):** Pb in the E seam is in the range of 1 to 121 ppm. Five of six profiles studied have < 25 ppm Pb. However, locally Pb can attain relatively high concentrations. For example, one horizon (637-E) at site 637 has a Pb content of 121 ppm (**Fig. 4.9**). Further investigation revealed that the extremely high Pb concentration in this interval is due to

the presence of a Pb-bearing mineral, crocoite ($PbCrO_4$, see **Section 4.5** and Li et al., 2001b for detailed discussion). Vertically, **Figure 4.9** illustrates that, in general, the high Pb zones appear to be at both the top and bottom third of the seam.

As shown in **Figure 4.9**, Pb in the Main seam is generally <10 ppm except in the bottom layers in the split lower subseam (DH 755), where crocoite was found and Pb locally reaches 28 ppm (Li et al., 2001b). In the case of the seam split, Pb tends to increase with depth in the upper seam as observed in the north (DH 755) and south (MU and 819) parts of the study area of the Main seam. In the unsplit thick Main seam (DH 703), a relatively high Pb zone appears at or near both the top and bottom layers.

**Sulphur (S):** S in the E seam ranges from 0.13% to 0.43%. In five of six profiles investigated (**Fig. 4. 10**), S was enriched in the top layer and decreased dramatically for the upper two-thirds of the seam (**Fig. 4.10**) although in some samples relatively high S concentration is also found in the lower one-third of the seam.

In contrast to the E seam, S generally increases with depth (**Fig. 4.10**) in the unsplit Main seam (DH 703), but in the case of the Main seam split, no systematic variation trend was observed. S in the Main seam ranges from 0.27% to 1.1%.

**Antimony (Sb):** Sb in the E seam is < 1.5 ppm in all six profiles studied. Relatively high Sb content appears in both the top and bottom layers (**Fig. 4.11**); in contrast, the middle part of the seam has a low Sb content (<0.2 ppm).

Sb in the Main seam is < 2ppm, and shows a similar vertical variation pattern to the E seam. As a rule, the lower subseam has higher Sb than the upper subseam (**Fig. 4.11 box I and J**).

Three roof and floor rocks of the E seam have Sb content ranging from 0.64 to 1.61 ppm, which is similar to their counterpart in the Main seam.

**Selenium (Se):** Se is the only HAP in Greymouth coals that shows significant enrichment (enrichment factor of 9.2, see Table 4.2) relative to the average Se in the upper crust (0.08 ppm). Se in the E seam is < 4 ppm and mostly < 1 ppm in all six profiles studied (**Fig. 4.12**). Se tends to be enriched in the top and/or bottom layers of the E seam, with lowest Se content present in the middle of the seam in most cases. Se in the Main seam is < 2 ppm and is lowest in the middle of the seam (**Fig. 4.12**).

The Se content in roof and floor rocks range from 0.58 to 1.28 ppm in the E seam whereas it ranges from 1 to 2 ppm in the Main seam.

**Uranium (U):** U concentration is <2 ppm in the E seam and <2.2 ppm in the Main seam. U generally follows the same trend as Se in both the E and Main seams (**Fig. 4.13**). The averaged U in both the Main (0.1 ppm) and E (0.4 ppm) seams are significantly lower than what is found in the upper crust (2.5 ppm).

### 4.2.2 Rare Earth Elements (REE) and Th

Rare earth elements (REE) are discussed here because of their significance in determining the source of inorganic matter (including ash-associated trace elements) in the coal. The rare earth elements are traditionally divided into two subgroups: those from La to Sm (i.e., lower atomic number and masses) are referred to as light rare earth elements (LREE) and those from Gd to Lu (higher atomic number and masses) are referred to as heavy rare earth elements (HREE). In general, both the light rare earth elements (LREE) and heavy rare earth elements (HREE) tend to be enriched in the top and bottom portions of the seam and depleted in the mid-seam (**Figs. 4.14 and 4.15**) areas.

**Thorium (Th):** Th in both the E and Main seams ranges from 0.1 to 4 ppm. Th tends to be enriched at or near the bottom of the seam (**Fig. 4.16**), as well as in the top of the seam (**Fig. 4.16 box c and f**) in two locations (O/C2 and 283).

### 4.2.3 Other Trace Elements

**Barium (Ba), Rubidium (Rb) and Strontium (Sr):** Ba, Rb and Sr are, in most cases, present only in low concentrations. Mostly these elements are below the DL for XRF in both the E and Main seams; an exception is the top and/or bottom layers where abundances are higher: i.e. Ba (10 ppm to 300 ppm), Rb (30 to 200 ppm) and Sr (20 to 700 ppm). Vertically, Ba, Rb and Sr generally vary sympathetically in both the E and Main seams (**Figs. 4.17 to 4.19**).

**Zinc (Zn) and Zirconium (Zr):** Zn (2 to 40 ppm) and Zr (1 to 140 ppm) follow the same variation trend (**Figs. 4.20 and 4.21**) as Rb and Sr.

## 4.3 Lateral Variation of Trace Elements

Almost all of the coal samples were analysed by XRF for selected trace elements. However, because most trace elements investigated in this study fell below XRF detection limits (DL), and also due to limited funding, only selected samples were analysed by INAA to obtain more precise trace element data. Where available, the following discussion will be based on INAA data; otherwise, XRF data will be used for the discussion of elemental abundance and distribution. Bear in mind that for the discussion of lateral variation of trace elements, only weighted seam average concentrations of trace elements will be used, unless stated otherwise. For example, the weighted seam average concentration of Se in profile 637 is calculated using the Se concentration in different sampled positions in the profile and the thickness they represent at that specific position. The lateral variation of trace elements are described to show how the weighted seam average concentrations vary along two directions (i.e. cross

section): (1) from the east (sites OPC and O/C2) to the centre (site 2A-2B) to the west (site P532A), and (2) from the north (site 637) to the centre (site 2A-2B) to the south (site 283).

### 4.3.1 HAPs, S, Cl and F

**Arsenic (As):** The E seam average arsenic is 0.36 ppm. Thirty-three samples covering six profiles of the E seam, as previously described, were analysed by INAA. All thirty-three samples including two parting samples have < 0.71 ppm arsenic and show less variation than what is found in the Main seam.

**Figure 4.22** displays the lateral variation of average arsenic in the E seam. In terms of the weighted seam average for arsenic content in the E seam, arsenic tends to decrease slightly from the basin centre (0.7 ppm) towards both the north (0.5 ppm) and west (0.5 ppm) margins. However, arsenic decreases rapidly from the centre (0.7 ppm) towards both the south (<0.1 ppm) and east margins (0.1 to 0.2 ppm).

The average arsenic in the Main seam varies from 0.1 ppm to 1.5 ppm, and it appears that the north part (DH 703 and DH 755) has higher arsenic (1.4 to 1.5 ppm) than the south part (MU and DH819 with 0.1 to 0.4 ppm).

Of the twenty-three coal samples from the north part of the Main seam, arsenic concentrations show a wide range of variations from 0.12 ppm to 21.16 ppm. Eighteen out of 23 coal samples have arsenic concentrations of less than 3 ppm; in contrast, three of the remaining five samples have arsenic >15 ppm. The arsenic contents in five roof and floor rock samples are in the range of 1 to 2 ppm.

Six out of seven coal samples from three locations of the Main seam in the southeast have As < 0.5 ppm, whereas only one out of seven coal samples has 1.22 ppm arsenic.

**Chlorine (Cl):** Cl in most parts of the E seam is <0.23%, and increases towards the south margin where Cl is 0.38% (**Fig. 4.23**).

For the Main seam Cl is at much lower concentrations (0.05% to 0.07%) than in the E seam (0.25% to 0.34%), and rarely exceeds 0.1%.

**Cobalt (Co):** Average Co in the E seam is 10 ppm. **Figure 4.24** displays the lateral variation of Co in the E seam. Co tends to increase from the centre (7 ppm) towards all margins, north (12 ppm), west (13 ppm) south (12 ppm) and east (12 ppm).

Average Co in the Main seam varies in the much wider range of 7 to 45 ppm. Co in the north part is 17 to 45 ppm, and in the south part is 7 to 30 ppm.

**Chromium (Cr):** Average Cr in the E seam is 9 ppm. Cr tends to vary in a narrow range of 4 to 11 ppm (**Fig. 4.25**). Cr decreases from the centre (9 ppm) towards both the north (8 ppm) and south (4 ppm), but increases from the centre (9 ppm) towards both the west (11ppm) and the east (11 ppm) margins.

Cr in the Main seam is at a lower average concentration (1 to 2 ppm) than in the E seam. Cr in the north part is around 2 ppm and in the south part it is 1 to 2 ppm.

**Fluorine (F):** Average F for all E seam samples analysed is 27 ppm. F tends to increase from both the east (24 ppm) to the centre (31 ppm) and west (42 ppm) of the study area, and tends to decrease from the centre (31 ppm) towards both the north (17 ppm) and south (22 ppm) (**Fig. 4.26**).

F in the Main seam varies in a similar range (18 to 42 ppm) to the E seam, and seems to increase from the north (18 to 19 ppm) to the south (30 to 42 ppm) margin.

**Mercury (Hg):** Average Hg of the E seam is 34 ppb. Hg contents in 33 E seam samples are less than 200 ppb. Thirty out of 33 samples have <90 ppb Hg, with three samples having 116 to 193 ppb. **Figure 4.27** shows that the seam average Hg content increases from both the east (9 to 24 ppb) and west (29 ppb) margins towards the centre (43 ppb), but decreases from both the north (47 ppb) and south (54 ppb) towards the centre.

Seven coal samples from three locations from the south part of the Main seam have Hg concentration variations restricted to a narrow range from 59 to 102 ppb. There are no Hg data for the north part of the Main seam.

**Manganese (Mn):** Average Mn level in the E seam is 28 ppm. **Figure 4.28** shows that Mn in most of the E seam varies in a range of 3 to 18 ppm. The exception is in the south part of the E seam where Mn is over 100 ppm.

Mn in the Main seam tends to increase from the north (8 to 13 ppm) towards the south (6 to 34 ppm).

**Nickel (Ni):** Average Ni for the E seam is 24 ppm. **Figure 4.29** shows that Ni increases gradually from the north (18 ppm) to the centre (21 ppm) and to the south (30 ppm). Ni also seems to increase from the east (22 ppm) to the west (29 ppm).

Ni in the Main seam also tends to increase from the north (7 to 8 ppm) to the south (11 to 40 ppm).

**Lead (Pb):** Average Pb in the E seam is 6 ppm. Pb tends to be constant at 4 to 5 ppm (**Fig. 4.30**) from the east (5 ppm) to the centre (4 ppm) and to the west (5 ppm). But Pb increases from the centre (4 ppm) towards both the south (6 ppm) and north (12 ppm) margins where the Pb-bearing mineral crocoite was found (Li et al., 2001b, also see section 4.5).

Pb in the Main seam is at a lower concentration than in the E seam, but slightly increases from the north (2 to 5 ppm) towards the south (5 to 6 ppm).

Although the concentration is generally low in both seams, Pb was found locally enriched in some intervals such as in sample 637-E (121 ppm), and >20 ppm at several other intervals in 283-A, 283-M of the E seam. Pb is >20 ppm at several sampled intervals such as 755-S, 755-T in the Main seam.

**Sulphur (S):** S content (0.25% to 0.34%) in the E seam appears to increase from the east (0.28%) to the west (0.33%) and also from the north (0.25%) towards the south (0.34%) (**Figure 4.31**).

Average S content for the Main seam decreases from the north (0.44% to 0.57%) towards the south margin (0.39% to 0.4%).

**Antimony (Sb):** Average Sb in the E seam is 0.15 ppm and varies in a narrow range of 0.11 ppm to 0.24 ppm in the six profiles studied (**Figure 4.32**). Sb increases from the east (0.12 ppm) towards the west (0.24 ppm) margins, and also increases from the north (0.11 ppm) towards the south (0.15 ppm). Of the 34 samples from six profiles, twenty-eight samples have a Sb content of less than 0.3 ppm, whereas only 3 parting-related samples have 1 to 1.32 ppm Sb.

Sb in the Main seam is generally well below 0.1 ppm in the north part of the Main seam deposit, as observed in DH 703 and DH 755. However, Sb seems to be elevated, at least from one location (DH 819) in the southeast part of the Main seam study area, with 0.7 ppm Sb.

**Selenium (Se):** Average Se of the E seam is 0.8 ppm. Se increases from the north (0.7 ppm) towards the south (1.2 ppm) and also increases from the east (0.5 ppm) towards the west (0.9 ppm) (**Figure 4.33**).

Average Se for the Main seam also increases from the north (0.3 ppm) towards the south (0.8 to 0.9 ppm).

**Uranium (U):** Average U of the E seam is 0.36 ppm. **Figure 4.34** shows that U gradually increases from the east (0.3 ppm) towards the west (0.48 ppm). But U tends to decrease from the centre of the study area (0.45 ppm) towards both the north (0.24 ppm) and south (0.28 ppm). Compared with the E seam, U in the Main seam is generally at very low concentrations of 0 to 0.14 ppm.

### 4.3.2 Rare Earth Elements (REE) and Th

Rare earth elements (REE): In the E seam, the average LREE (light rare earth elements La to Sm) is 19 ppm and increases from the east (19 ppm) towards the west (32 ppm), but decreases from the centre (22 ppm) towards both the north (12 ppm) and south (12 ppm) (**Fig. 4.35**).

In contrast, the average HREE (heavy rare earth elements Gd to Lu) tend to increase from the central part of the study area (0.5 ppm) toward both the east (1 to 1.5 ppm) and west (1.1 ppm) margins of the E seam (**Fig. 4.36**). HREE also increase slightly from the south (0.4 ppm) towards the north (0.7 ppm) margins.

In the Main seam, LREE is relatively higher in the northern part (4 to 7 ppm) of the study area than in the southern part (2 to 3 ppm). Likewise, HREE is also higher (0.3 to 0.4 ppm) in the north part than what is found in the south part (0.1 to 0.2 ppm) of the study area.

**Thorium (Th):** Average Th in the E seam is 1.4 ppm. While Th tends to increase (**Fig. 4.37**) from the east (1.3 ppm) towards both the centre (2 ppm) and west margins (2.1

ppm), Th decreases from the centre (2 ppm) to both the north (0.7 ppm) and south (1.2 ppm). Th appears to vary at the same pattern as LREE.

Th in the Main seam is at the relatively lower concentration of 0.2 to 0.6 ppm. The north part seems to have higher Th (0.4 to 0.6 ppm) than the south part (0.2 to 0.3 ppm) of the Main seam.

### 4.3.3 Other Trace Elements

**Boron (B):** B has long been recognised as an essential nutrient for plant growth. As early as the 1940s, Rafter (1945) noted high B content (up to 1.5% B in Waikato coals) in all major New Zealand coals. Ross (1957) and Kear and Ross (1961) also reported high B levels in Waikato coals. Boron is often found in New Zealand coals at levels significantly above the world mean. However, high B coals in New Zealand are mainly present in the Waikato coal fields, and to a lesser extent, in coals from the Southland region. High B is one of the characteristics that distinguish New Zealand coal from most other coals around the world. Further study revealed that most, if not all, high B coals are associated with marine invasions and/or brackish water environments. Soong and Berrow (1979) believed that B in New Zealand tends to be at a higher concentration in subbituminous coals.

The Cl/Br ratio is a useful indicator of depositional environment. On average, the Cl/Br ratios range from 700 to 2000 in the E seam (**Table 4.3**) and from 200 to 500 in the Main seam (Cl/Br in seam water on average is around 290), indicating that more Cl cations (e.g., high salty) are present in the E seam basin system than the Main seam depositional environment.

In the Greymouth coal beds, only a few samples from the E seam were analysed in this study for B content, which is in the narrow range of 48 to 61 ppm (on dry coal basis, **Table 4.1**). Such a low B content in the Greymouth coal is very unlikely to cause any environmental concerns for this coal. There are no B data from the Main seam coal. Kear and Ross (1961) report 0.85% $B_2O_3$ in ash (equivalent to 190 ppm of $B_2O_3$ in coal). The

B contents on an ash basis are 460 ppm, 1500 ppm, 490 ppm in sample 2A, 2B and P532A, respectively. In contrast, B in the Waikato coal ash is in the range of 2700 ppm to 7000. Kear and Ross (1961) reported 4.8% $B_2O_3$ in run of mine coal ash in Waikato coals. In fact, it is not uncommon to find $B_2O_3$ in coal from the central Waikato coal basins ranging from 910 to 1790 ppm (Kear and Ross, 1961). Stockton coal (bituminous Brunner Coal Measures, Westland) was transgressed by marine sediments and thus a high B content is to be expected. However, these coals only have a reported B content of 160 ppm (ash basis).

**Barium (Ba):** Average Ba in the E seam is 61 ppm. Ba in the E seam appears to increase from the east (67 ppm) to the west (92 ppm), but decreases from the centre (67 ppm) towards both the southern (28 ppm) and northern (48 ppm) parts of the study area (**Fig. 4.38**).

Ba in the Main seam is at a much lower concentration than in the E seam, and decreases from the north (13 to 18 ppm) towards the south (1 ppm).

**Rubidium (Rb):** Average Rb in the E seam is 12 ppm. Rb (**Fig. 4.39**) appears to increase from the east (12 ppm) towards both the centre (17 ppm) and west (17 ppm), but decrease from the centre (17 ppm) towards both the north (4 ppm) and south (2 ppm). Rb concentration in the Main seam is below the XRF detection limit (2 ppm).

**Strontium (Sr):** Average Sr in the E seam is 48 ppm. Sr has the lowest concentration in the central part of the study area, but increases rapidly from the centre part of the study area (22 ppm) towards both the east (90 ppm) and west (50 ppm) (**Fig. 4.40**).

In contrast to the E seam, Sr in the Main seam has a much lower concentration (<10 ppm), and appears to decrease from the north (8 to 10 ppm) towards the south margin (1 to 2 ppm).

**Cesium (Cs):** Cs in the E seam varies in a narrow range from 2 to 5 ppm (**Fig. 4.41**). With such a narrow range, it is difficult to ascertain any spatial variation variability.

**Scandium (Sc):** Sc in the E seam is 1.4 ppm, and tends to increase from the east (1.2 ppm) to the west (2.3 ppm), but decreases from the centre (2 ppm) towards both the north (0.8 ppm) and south (0.9 ppm) margins (**Fig. 4.42**).

Sc in the Main seam is at a lower concentration (0.1 to 0.4 ppm) than that found in the E seam, and appears to decrease from the north (0.3 to 0.4 ppm) towards the south (0.1 ppm).

**Zinc (Zn):** Average Zn in the E seam is 10 ppm, and Zn tends to increase from the centre (5 ppm) of the study area towards all areas (8 to 18 ppm) (**Fig. 4. 43**).

Zn appears to increase from the north (3 ppm) towards the south (6 to 12 ppm) in the Main seam.

**Zirconium (Zr):** Average Zr in the E seam is 7 ppm (**Fig. 4.44**). The high Zr zone is always in contact with inorganic parting, roof or floor rocks.

## 4.4 Trace Element Modes of Occurrence

In a study of trace element mode of occurrence of US coals, Finkelman (1980) investigated the distribution of most trace elements using SEM-EDXA analysis. However, as pointed out earlier, most trace elements in Greymouth coals are below the detection limit for SEM-EDXA (usually 0.5% to 1% depending on the specific element). Therefore, it is not always possible to locate directly the hosts for the trace elements by such traditional methods. Therefore, some alternative approaches were used to determine the mode of occurrence for the trace elements in Greymouth coals. In this study, the evidence from five different methods has been combined to determine the modes of

occurrence of trace elements in the coal. This evidence is from (1) direct SEM-EDXA observation of trace elements in coal when possible, (2) the behaviour of trace elements in the float sink experiments, (3) the behaviour of trace elements in the sequential leaching tests, (4) trace element contents in minerals and raw coal from INAA analysis, and (5) inter-element correlation based on the statistical correlation of 80 whole coal analyses from both the E and Main seams. With all the supporting evidence from those five analytical methods and approaches, conclusions regarding possible modes of occurrence of trace elements in coal can be drawn more confidently than if only one or a few methodologies to be employed. The following sections first describe the observations made from the different techniques used in the course of this study, and then determine and discuss the modes of occurrence of individual elements by combining those data and observations.

### 4.4.1 SEM-EDXA Observations

Because of the low abundance of trace elements in the Greymouth coals, most of the trace elements studied fell below the detection limit (DL) of conventional analytical equipment (e.g. SEM-EDXA or XRD). Thus, only a few trace elements were detected directly using SEM-EDXA. For example, Zr was detected in clay and zircon (**Figs. 4.45a to 4.45c**), Cr, Ti and Th in clays, Cr and Pb in crocoite; REE in apatite and monazite (**Figs. 4.46a and 4.46b**); and Th was detected as inclusions in quartz grains (**Fig. 4.47**); Ti was detected associated with clays (**Figs. 4.48a to 4.48c**).

### 4.4.2 Float-sink Behaviour of Trace Elements in Coal

Float-sink experiments were performed on whole coal samples to determine whether low trace elements were associated with mineral matter or organic matter. The procedures of float-sink experiment were described in **Section 2.2.3**. In order to determine whether a trace element is enriched in float or sink fractions, an enrichment index (EI) is used to define concentrations of trace elements in sink and float fractions. The EI is calculated by

using the following equation:

$$EI = C_{fract}/C_{feed} \quad (1)$$

where $C_{fract}$ represents trace element concentration in the float or sink fraction after separation, and $C_{feed}$ represents trace element concentration in the feed coal. If EI > 1, it means the element is enriched in this fraction. If EI < 1, it means the element is depleted in this fraction. **Table 4.4** and **Figure 4.49** illustrate that almost all elements, except S and Ni have EIs > 1 in the sink fraction, indicating an enrichment in the sink fractions. Some elements (Th, Se, Nb, As, S, Ni, Pb and Cl) have an EI of 0.6 to 1 in the float fractions in all samples (P532A, P532B, 2A, 2B), and V, La, Ga, Rb and Zn also have EIs close to 1 in the float fractions, but only for those samples from the bottom of the seam (P532B and 2B). The trace elements with EF close to 1 in the float fractions are not depleted significantly in the float fractions, suggesting that these elements show no preferential association with organic matter or mineral phases in the coal.

However, EI alone is not always a reliable indicator of whether an element is enriched in float or sink fractions. In contrast, the absolute weight percentages of an element in the float or sink fractions are the more accurate parameters to indicate whether a specific element is enriched in the float or sink fraction. Based on trace element concentrations in the feed coal before separation and in the float and sink fractions after separation, as well as weight% (wt%) of float and sink fractions after separation, an absolute mass balance of each element of interest can be calculated. The fractional percentages of trace elements in the float and sink fractions are given in **Table 4.5** and **Fig. 4.50**). From this data, trace elements have been categorised into three groups.

The first group has pronounced enrichment in the sink fractions. Generally up to 99 wt% of the total elemental content of this group of elements are present in the sink fractions (**Fig. 4.50**). The order of trace elements from the highest enrichment to the least enrichment is: Rb, Sr, Ba, Y, Cr, Zn, Zr, Th, F, REE, Ga and V.

The second group elements include Cl, S, Se, As and Ni. This group is characterised by elevated concentrations in the float fractions. In terms of total trace elements in coal, 30% to 93% of Cl, 30% to 90% of S, 16% to 64% of Se, 43% to 64% of As, and 39% to 73% of Ni are present in the float fractions (**Table 4.5**). Elements in this group are most likely associated with organic matter.

The third group of elements includes Pb and Nb with no clear enrichment in the float or sink fractions. For example, Pb, in a sample of coal from the top of the E seam (2A and P532A) tends to have 63% to 82% of the Pb in the sink fraction, whereas coal samples from the bottom of the seam only have 22% to 34% of the Pb in the sink fraction.

### 4.4.3 Trace Element Contents in Minerals

As most trace element concentrations in the Greymouth coals are very low (**Appendices 7** and **8**), direct identification of the trace element hosts is not possible. The determination of the exact modes of occurrence of these trace elements turns out to be a great challenge. In order to overcome this barrier and determine the trace element contents in minerals, an attempt was made to determine what trace element concentrations are in all the major mineral phases, which are deemed to be significant hosts for trace elements. Ten mineral samples (extracted from raw coal, or obtained from low temperature ash) were analysed by INAA following the same procedures as whole coal analysis. These ten mineral concentrates include 7 clay mineral samples from different sampling localities, two carbonates (one ankerite and one siderite) and one pyrite. All these mineral concentrates have a purity of >95%. Clays and quartz compose the bulk of the mineral matter in both the E and Main seams. The only other mineral group that can possibly be a significant host for trace elements is the carbonates (mainly siderite and ankerite) in the E seam and pyrite in the Main seam (see Chapter 3 for mineralogy details). The crystal structure of quartz will not accommodate a significant amount of any element other than Si-O. The trace element analysis of a quartz sample (283-I1) in this study confirmed that only Co and W are significantly enriched in quartz in relation to the whole coal data (see **Appendix 8**). Hence, the contribution of trace elements (except Co and W) from quartz is

negligible. Therefore, in terms of trace element contributions from minerals, only clays plus carbonates for the E seam and clays plus pyrite for the Main seam need to be considered as significant contributors. Clay minerals compose approximate 70% of the total mineral matter in both the E and Main seams. In addition to the bulk clays, the clays deemed to be formed at late stages (tabular clay, needle-shape clay and big clay conglomerate) were handpicked to determine their trace element contents. It was found that the late-stage clays (samples C-TB, C-ND in **Table 4.6**) have far lower trace element contents than the clays formed during the early coal formation processes (samples C-R, C-MU, C-PA, C-PB, C-6M in **Table 4.6**).

### 4.4.4 Leaching Behaviour of Elements

#### 4.4.4.1 Introduction to Sequential Acid Leaching

A sequential leaching test, following procedures described by Palmer et al. (1993), was undertaken to investigate where trace elements occurred in coal; in other words, indirect methods were used to determine the modes of occurrence of trace elements. Three E seam composite samples from three underground locations of the Strongman No. 2 Mine were subjected to leaching tests to determine the modes of occurrence of trace elements in this coal. The coal was sequentially leached in 1N ammonia acetate (AmAc), 2N hydrochloride (HCl), 48% hydrofluoric acid (HF), and 2N nitric acid ($HNO_3$). A subset of leached solid residue samples and resultant leachates were analysed by INAA (for solid) and ICP-MS, ICP-AES (for leachate). Trace element concentrations in the coal samples before leaching and the residual fractions after every leaching step are given in **Appendix 9**. Trace element concentrations in all the resulted leachate samples analysed by ICP-MS and ICP-AES are given in **Appendices 10** and **11** respectively. After the leaching test, data were transformed into leached weight percentages following procedures similar to those described by Palmer et al. (1993) and Mroczkowski et al. (1998). The sequential leaching test is theoretically based on the following assumptions: (1) in the first step, 1N ammonia acetate selectively removes all the trace elements weakly-bonded with the coal matrix, (2) 2N HCl then selectively leaches all trace

elements associated with the carbonates and monosulphides, (3) then 48% HF selectively leaches all trace elements associated with the silicates, and lastly (4) 2N $HNO_3$ removes all trace elements associated with the disulphides. Based on the above assumptions, the leached percentage of each trace element can be calculated at each step.

#### 4.4.4.2 Leaching Behaviour of Major Elements

The major elements Al, K, Ti, Na, Fe, Ca, Mg, Mn and P were analysed and the proportion of each element, removed at each leaching step, was calculated (**Table 4.7** and **Fig. 4.51**).

As expected, 85% to 100% of the total Al and K, 40% to 80% of Ti and 45% to 55% of Na were leached by the HF, confirming their affinity with the silicates (clays and quartz) and consistent with the mineralogical results. The majority of the Al, K, Ti and Na was expected to be removed by HF because these elements are commonly hosted in aluminosilicates, namely clay minerals (mainly kaolinite, illite, etc), which comprise the bulk of the coal minerals in the Greymouth coals. The leaching test results suggest that 45% to 55% of the total Na is associated with silicates (**Fig. 4.51**). In addition, 5% to 10% of the Na was soluble in $NH_4Ac$ and HCl, suggesting that some of the Na is present as salt (NaCl) and associated with the carbonates. Salt (NaCl) occurrence was confirmed by SEM-EDXA observation.

Around 80% of the Ca, 75% to 95% of the Fe, 55% to 65% of the P, 35% to 80% of the Mg and 50% to 100% of the Mn were removed by HCl, confirming their primary association with carbonates (siderite and calcite) and phosphates. This is consistent with the observation in the mineralogical study (Li et al., 1999a, 2001a). It should be pointed out that the phosphate minerals apatite [$Ca_5$ ($PO_4$,$CO_3$) $_3$(F, OH, Cl)], monazite [(Ce, La, Nd, Th, Sm)($PO_4$, $SiO_4$)] and crandallite [$CaAl_3(PO_4)_2(OH)_5H_2O$] were identified in the coal samples under SEM-EDX. These phosphate minerals are present as discrete minerals or a mineral group associated with carbonates and, in some cases, with clays.

Therefore, it is not surprising to see that a substantial portion of the Ca was accounted for by phosphates.

### 4.4.5 Silicate-Associated Elements

This group of elements includes some HAPs (As, Hg, Sb, Be, Cr, U) and traditional silicate-associated elements (Rb, Sr, Sc, V, Li, Zr, W) as well as Ba, Tl, Cs, Sn, Mo, Hf and Ta.

**Arsenic (As):** Arsenic has long been recognised as a toxic element in the environment. Coal combustion is one of the important contributors of arsenic to the environment. Arsenic is believed to be present mostly in sulphides or adsorbed on to Fe-hydroxides or in clay (Reimann and Caritat, 1998).

The concentration of arsenic in coal samples in this study that underwent leaching tests ranged from 0.53 to 0.82 ppm. In the float-sink experiments, on average 48% of the arsenic was in the sink fraction (**Table 4.8**). The average total arsenic leached is 45%, with the range of 25% to 65%, indicating multiple modes of occurrence for arsenic. Arsenic leached by HF alone is on average 30%, with a range of 15% to 45%. Only a minor amount (5%) of the arsenic was leached by HCl and $HNO_3$ and no arsenic was removed by ammonia acetate. The leaching test results show that a substantial amount of arsenic (up to 45%) was removed by HF indicating an arsenic association with aluminosilicates (in this case, mostly clays). The arsenic content (INAA data) in raw coal and in minerals extracted from coal and LTA ash (see **Table 4.8**), may shed some light on the possible hosts of arsenic.

Arsenic is greatly enriched in two of the four mineral groups, clays and pyrite. Clay minerals and carbonates compose the bulk mineral matter of the E seam coal. Arsenic content in clay minerals is 6 to 8 ppm, and this mode of occurrence may account for the total arsenic in the E seam coal (< 0.8 ppm in the coal). No arsenic was detected in the

carbonates (ankerite and siderite) of the E seam. There is little to no pyrite in the E seam coal.

Interestingly, between 35% to 75% of the arsenic was not leached by any of the solvents. It was noted that 15% of the arsenic was removed by HCl indicating a possible carbonate or arsenate association. The float sink experiment shows that arsenic appears to be distributed evenly in the float and sink fraction for all three samples analysed. Two possible explanations are offered. One hypothesis is that arsenic has an organic association. The other explanation is that arsenic is associated with micron-sized clays, which are intimately dispersed in the coal matrix. Sulphides seem unlikely to be a significant mode of occurrence of arsenic in the E seam coal; instead, arsenic is primarily associated with silicates (clays), and some arsenic is also possibly associated with organic matter in the E seam coal.

In contrast, coal samples from the Main seam have higher arsenic contents (<0.2 ppm to 21 ppm) than the E seam. In the Main seam coal clay minerals and quartz are the major minerals with minor pyrite. Pyrite has 430 ppm arsenic and may account for only 20% of the total arsenic in coal. But the arsenic in the clays accounts for 15% to 70% of the total arsenic in the Main seam coal (**Table 4.8**). Therefore, arsenic is mainly associated with clays, and possibly some with organic matter; whereas some arsenic is associated with sulphide as widely reported in numerous studies (Duck and Himus, 1951; Mackowsky, 1982; Minkin et al., 1984; White et al., 1989; Finkelman et al., 1992; Ruppert et al., 1992; Huggins et al., 1993). Kolker et al. (2000) found that arsenic in three bituminous coals is dominantly in pyrite, but primarily associated with organics (as $As^{3+}$, or as arsenate) in another sub-bituminous coal.

**Barium (Ba):** Ba-bearing minerals were not directly detected under SEM-EDX in the coal because of their low abundance. However, $BaSO_4$ was detected in fly ash after combustion (see **Fig. 5.4** in Chapter 5). In the float-sink experiments, 77% to 98% of the Ba was in the sink fractions, suggesting a dominant mineral affinity. In the leaching tests,

on average 80% of the Ba was leached by HF, indicating a strong silicate association (**Table 4.8**). Furthermore, Ba was found to be enriched in clay minerals within the coal. The enrichment factor is in the order of tens to hundreds of times the Ba concentration found in the coal.

Compared with the average Ba concentration of 48 to 143 ppm in the E seam coal, Ba contents in clay range from 692 to 1357 ppm; this accounts for >60% of the Ba (**Table 4.8**) in the coal. No Ba was detected in ankerite and siderite. This strongly indicated that Ba is predominantly associated with clays.

The Ba content in the clays of the Main seam range from 226 to 461 ppm, which accounts for 10% to 55% of the total Ba in the coal (average Ba concentration only 0.5 to 13 ppm). No Ba was detected in any of the pyrite minerals examined. Ba has good correlation (r = 0.9) with $SiO_2$, $Al_2O_3$, $K_2O$, $P_2O_5$ and REE (**Figs. 4.52 to 4.54**). Therefore, Ba is mainly associated with clays, and to a lesser extent, with REE phosphates (crandallite). Ba variation closely follows the same variation trend as Rb and Sr in the Main seam, and those elements are well correlated with each other ($r$ = 0.6 to 0.9). There are two possible explanations: (a) Ba is hosted in clays as an elemental replacement of K, Na or Ca, or (b) Ba is present as fine-grained barite ($BaSO_4$) or witherite ($BaCO_3$), but as fine inclusions in silicates (mainly clay minerals), so that they would fail to be leached by the acids until the silicates were dissolved by HF. Newman (1988) suspected crandallite was a major host for Ba in both the Paparoa and Brunner coals.

Filby et al. (1977) also found that 76% of the Ba was inorganically bound. Nicholls (1968) speculated that Ba is associated with Ba-bearing minerals (such as barite) in their studies. Finkelman (1981) found Ba occurred predominantly as carbonates in bituminous Alaskan coal, but occurred exclusively as sulfate in Beulah lignite.

**Beryllium (Be):** Be ranges from 1.2 to 1.6 ppm (ICP-MS data). Thirty to 55% of the total Be was removed by HF with an average of no more than 5% Be leached by any of the other three solvents (**Table 4.9**), indicating a significant silicate association. However, 40% to 65% of total Be remained unleached and an inverse Be variation with ash content strongly suggests a major organic association. Be (with atomic no. of 4) is very difficult to detect by conventional SEM-EDX and microprobe. However, abundant indirect evidence in the literature suggests a strong organic affinity for Be, by the observation of reverse variation of Be with ash yields (Razdorozhniy, 1967; Miller and Given, 1978) and by consistent float-sink experiment results (Horton and Aubrey, 1950; Gluskoter, 1977; Finkelman, 1981). Zubovic (1966) found Be concentrated in the near source margins in the Illinois coal basin and attributed this to organic chelating of Be to form stable and insoluble organic compounds.

**Chromium (Cr):** In the float-sink experiment, 58% to 92% of the Cr was in the sink fractions. This indicates a strong association with minerals in the coal. Clays are the predominant minerals in the coal; furthermore, Cr was also found in clays under SEM-EDXA. In the leaching tests, on average 55% of Cr was leached by HF, suggesting a silicate association.

The clays from the E seam contain 110 to 175 ppm Cr and could account for >90% of the total Cr (**Table 4.9**) in the coal (10 to 17 ppm). Only 11 ppm Cr was detected in siderite, which accounts for 4% of the total Cr. No Cr was detected in ankerite.

The clays from the Main seam have 140 to 315 ppm Cr, and could account for more than 70% of the total Cr in the coal (4 to 15 ppm). Cr in pyrite is only 8 ppm and may account for 1% of the Cr in the coal.

Given the low Cr concentration in carbonates and sulphides, these two types of modes of occurrence of Cr (carbonates or sulphides) are only minor (1 to 4%). This is also consistent with the leaching test results. Therefore, there is no doubt that the association

with clay minerals is the major mode of occurrence of Cr. Good correlation of Cr with $Al_2O_3$ and $K_2O$ also supports a clay association (**Figs. 4.52 to 4.53**).

Another mode of occurrence of Cr, crocoite ($PbCrO_4$), was observed in both the Main and E seams (see also Li et al., 1999b, 2001a). There is close correlation between Cr and Pb, but not between Pb and S, suggesting that crocoite is one of the significant modes of occurrence of Pb in these coals. Further discussion of crocoite can be found in **Section 4.5.**

In a study of US bituminous coals, Huggins et al. (2000) reported that Cr occurs principally in two forms: (1) mainly associated with macerals [where it is believed to occur as a small particles in an oxyhydroxide phase (CrO(OH))] and not readily leachable by any reagent, (2) to a lesser degree associated with illite. In addition, <5% of Cr is in the form of chromian magnetite and sulphides in one coal sample.

**Caesium (Cs):** Forty to 55% of the Cs was removed by HF, and 30% to 50% of the Cs was leached by HCl, suggesting multiple association with silicates and carbonates.

Cs in the clays of the E seam ranges from 30 to 140 ppm and may account for 90% of the total Cs in the coal. Cs in the ankerite is 9 ppm, and probably accounts for <10% of the total Cs in the coal (**Table 4.9**). No Cs was detected in siderite. Therefore, Cs is mainly associated with clays, and to a lesser extent, with ankerite.

Cs in the clays of the Main seam is 6 ppm, and may account for >70% of the Cs in the coal (0.1 to 0.3 ppm). No Cs was detected in pyrite. Therefore, clays are the dominant mode of occurrence of Cs in the coal. Cs has good correlation with $Al_2O_3$ (r=0.8) and $K_2O$ (r=0.9), also supporting a clay association of Cs (Figs. 4.52 and 4.53). The data of Gluskoter et al. (1977) and Finkelman (1981) also suggested an inorganic association of Cs. However, Filby et al. (1977) reported that 96% of the Cs in their sample was organically bound.

**Fluorine (F):** More than 80% of F is on average found in the sink fractions of float-sink tests, clearly suggesting a major mineral affinity. F is well-correlated (r = 0.8) with $Al_2O_3$, $P_2O_5$ and REE (**Figs. 4.52 and 4.54**). These associations also support the idea that F is associated with clays and phosphates. In addition, F was detected in the phosphates (perhaps fluorapatite) under SEM-EDXA. F can readily substitute for $OH^-$ in clays and micas (Wedepohl, 1972) and may be associated with these minerals (Finkelman, 1981; Beising and Kirsch, 1974). F is also believed to occur as fluorite (Lessing, 1934) and fluorapatite (Durie and Schafer, 1964; Swaine, 1975).

**Hafnium (Hf):** A range of 10 to 35% of Hf was removed by HF, suggesting a silicate association. The low percentage (30 % to 50%) total Hf removed in the leaching tests suggests that Hf has a major organic association in addition to being associated with silicates. Another possible occurrence of Hf is in insoluble phases, such as zircon. Hf was detected in zircon inclusions in the quartz grain (see following discussion on Zr).

Hf in clays of the E seam is 6 to 8 ppm, and could account for 65-85% of the total Hf in the coal (**Table 4.9**). No Hf was detected in the carbonates. Therefore, clays are the major host of the Hf in the E seam coal.

Hf in clays of the Main seam is 9 to 17 ppm, and could account for 80% of the total Hf in the coal. Hf in pyrite is 0.4 ppm, accounting for <1% of total Hf in the coal.

**Mercury (Hg):** Mercury levels in 8 major coal mines in New Zealand are less than 0.1 ppm (air dry basis) except Huntly East coal with Hg concentration of 0.12 ppm (**Table 4.1**). The Hg level in the E seam is lower than the US mean of 0.2 ppm and other overseas coals (Swaine and Goodarzi, 1995; Finkelman, 2000). In the E seam, Hg ranges from 0.06 ppm to 0.09 ppm (air dry basis).

Because of Hg's low concentration, it was not analysed in the leaching tests. The INAA analysis of coal and mineral concentrates extracted from coal shows similar distribution

trends to that of arsenic. Finkelman (1981) also observed a similar behaviour between Hg and As in US coals.

Finkelman (1995) states: "Mercury offers numerous challenges in determining its modes of occurrence...", because of the relatively low Hg concentration in coal and its high volatility (so it cannot be determined in the coal ash). There are few data about the modes of occurrence of Hg in coal because of these difficulties.

Based on US Geological Survey's COALQUAL database, O'Neil et al. (1999) stated "Strong indirect geochemical evidence indicates that a substantial proportion of the mercury in US coals is associated with pyrite occurrence. This association of mercury and pyrite probably accounts for the removal of mercury with the pyrite by physical coal cleaning procedures. Data from the literature indicate that conventional coal cleaning removes approximately 37% of the mercury on an equal energy basis, with a range of 0% to 78%...".

However, this is apparently not the case for the Greymouth coals. The Hg content in clays of the E seam is 830 ppb, and could account for >70% of Hg in the coal. Hg in siderite is 545 ppb, and could account for 30% of the total Hg of the coal. No Hg was detected in ankerite.

The Hg content is 900 to 2500 ppb in clays and 5681 ppb in pyrite of the Main seam (**Table 4.6**); Hg content in clays accounts for 90% of the total Hg content of the coal. Although Hg was detected at >5000 ppb in pyrite, this mode of occurrence only accounts for 10% of the total Hg of the coal.

The greater enrichment of Hg in pyrite (30 to 200 times) and clay in relation the coal clearly demonstrates that Hg has multiple modes of occurrence. While clays are the dominant hosts for Hg in both the E and Main seams, siderite in the E seam and pyrite in the Main seam also act as host sites for Hg.

**Lithium (Li):** Lithium is commonly present in mica lattices as an elemental replacement for K and Na and is also found in clay minerals, especially illite. In the Greymouth coals, 35% to 90% lithium was removed by HF, suggesting it is primarily associated with silicate and probably hosted by illite and minor micas.

**Rubidium (Rb):** In the float-sink experiments, on average 97% of the Rb was in the sink fractions (**Table 4.10**), suggesting a dominant association with mineral matter in the coal. In the leaching test, 50 to 90% of the Rb was leached by HF, clearly demonstrating that the majority of the Rb is associated with the silicates. Moreover, Rb in clays is 153 to 184 ppm, which accounts for 60-70% of the total Rb in the coal. Rb has a strongly positive correlation with $Al_2O_3$ (r=0.9), $K_2O$ (r=1.0) and $SiO_2$ (r=0.8), also supporting that Rb is associated with illite (**Fig. 4.52**). Therefore, as expected, Rb was found to be primarily associated with illite.

Rb geochemically behaves similarly to K (Goldschmidt, 1954) and the bulk of Rb in the crust is commonly found in K-feldspar and K-micas (such as illite), which is commonly present in coals. Accordingly, Finkelman (1981) speculated that substantial amounts of Rb in coal are probably in the illite and mixed-layer clays.

**Antimony (Sb):** The concentration of Sb in Greymouth coals ranges from 0.09 to 0.25 ppm. Sb was found to have the same behaviour as As in the leaching test. The total Sb leached in HF samples 2A and 2B is 20% and 50%, respectively. Because the majority of Sb leached was removed by HF, this indicates an association with silicates. However, in sample P532A, 30% of the Sb was leached by $HNO_3$ in addition to 25% by HF. This indicates that 30% of the Sb is associated with $HNO_3$-soluble sulphides (stibnite $Sb_2S_3$) and 20% of the Sb was associated with silicates. However, 45% to 80% of the Sb remained unleached, suggesting that a majority of Sb is either associated with organic matrix or present as sub-micron fine-grained clay minerals which are intimately dispersed in maceral and thus shielded by organic matrix, and essentially unleachable. Finkelman et al. (1990) noted 5% to 40% of the Sb was removed by HF from five of the seven bituminous coals they studied, but concluded that further work is necessary to determine

the modes of occurrence of Sb. There are actually very few data available on the modes of occurrence of Sb in coal. The only Sb-bearing mineral (ullmanite NiSbS) associated with coal was reported by Spencer (1910) from a carbonate vein of a UK coal bed. Dvornikov and Tikhonenkova (1973) also suggested a pyrite association for Sb. Finkelman (1981, 1995) reported that a substantial amount of the Sb may occur in pyrite and accessory sulphides (such as minute grains of $Sb_2S_3$ dispersed throughout the organic matrix).

Sb content in the clay minerals ranges from 1.61 to 11.2 ppm; the highest Sb is in the bulk LTA from the southeast part of the Main seam where Sb is relatively high. Pyrite has 1.15 ppm Sb, whereas no Sb was detected (it was below the detection limit of 0.01 ppm) in the carbonate concentrates (ankerite and siderite).

In the Main seam, Sb is enriched in the clay minerals with a range of 1.6 to 11.2 ppm; whereas in the E seam, the range is 2.4 to 3.2 ppm. Sb in the clays may account for 90% of the total Sb in the E seam and 80% in the Main seam coal (**Table 4.10**). Pyrite in the Main seam was also slightly enriched in Sb (1.15 ppm), and could account for 16% of the total Sb in the coal. No Sb was detected in the carbonates. Therefore, Sb is dominantly associated with silicates (clays) in both seams, although some Sb is associated with sulphides, probably as a solid solution in the pyrite of the Main seam. Sb is positively correlated with clay-related- elements V (r = 0.9), $TiO_2$ (r=0.7), $Al_2O_3$ (r =0.6) and $K_2O$ (r=0.6), confirming an association with clays (illite). Lack of correlation between Sb and S also supports that pyrite is not a major mode of occurrence of Sb in the Greymouth seams.

**Scandium (Sc):** In the leaching tests, 45% to 85% of the Sc was removed by HF (**Table 4.10**), indicating a strong silicate association. Sc in clays range from 3 to 17 ppm, and account for >65% and >75% of the Sc in the E and Main seam, respectively. Sc in carbonates is 1.4 to 2.2 ppm and accounts for 4-8% of the total Sc in the coal. Sc in pyrite is 0.5 ppm, accounting for <1% of the Sc in the coal (**Table 4.10**). Sc in the coal (except partings and coal next to partings and floor rocks) ranges from 0.1 to 4.6 ppm. This

suggests Sc is greatly enriched in clays. A clearly positive correlation of Sc with $SiO_2$ (r=0.8), $Al_2O_3$ (r=0.9) and $K_2O$ (r=0.8) also supports an association with clay (illite) (**Fig. 4.52**).

Sc is believed by some workers (Swaine, 1964; Borisova et al., 1977; Miller and Given, 1978) to be organically bound. In contrast, Sc is thought by others to be inorganically bound (Filby et al., 1977). A small proportion of Sc was even detected in clay and yttrium-bearing zircon (Finkelman, 1981) in US and Australian coals and phosphates (Frondel et al., 1968). However, Sc is predominantly associated with clays in the Greymouth coals.

**Strontium (Sr):** In float-sink experiments, 66% to 99% of the Sr is present in sink fractions, clearly suggesting an association with mineral matter. In the leaching tests, 65% to 90% of the Sr was leached by HF, strongly indicating that the majority of the Sr is associated with silicates. Moreover, Sr in clays ranges from 215 to 720 ppm in the E seam and 170 to 880 ppm in the Main seam. Sr in the clays accounts for >45% of the total Sr in the E seam coal and 55% to 75% in the Main seam coal (**Table 4.10**).

No Sr was detected in the carbonates of the E seam and the pyrite of the Main seam, although Sr was found to be fairly high in Australian coals (Brown and Swaine, 1964).
Sr is believed by Filby et al. (1977) and Nicholls (1968) to be inorganically bound. However, other workers (Miller and Given, 1978; Finkelman, 1981) believed that Sr is mainly complexed with organic matter. Newman (1988) suspected Sr occurs mainly in crandallite and carbonates based on inter-elemental correlation. Ward et al. (1999) concluded that Sr and Ba are strongly associated with the cleat-filling carbonate minerals in the Permian Gunnedah coalbed of New South Wales, Australia.

**Tantalum (Ta):** The total Ta leached was 35% to 50%, and most (25% to 30%) of the Ta leached is removed by HF, suggesting a silicate association.

Ta has a higher concentration in clays than that found in the carbonates and pyrite in the Greymouth coals, which also suggests a silicate association. Ta in clays of the E seam is 2 to 4 ppm, and could account for 75% to 90% of the Ta found in coal samples determined in this study. Ta in clays of the Main seam is 3 ppm, and could account for 30% to 85% of total Ta in the coal (**Table 4.10**). No Ta was detected in pyrite and carbonates. Therefore, Ta is predominantly associated with clays in the coal.

Solodov et al. (1975) and Gluskoter et al. (1977) reported a strong inorganic association of Ta in their studies. Kuhn et al. (1978) noted that Ta exhibits a very strong positive correlation with Ti and Hf. Finkelman (1981) reported Ta is primarily associated with detrital inorganic matter in coal.

**Thallium (Tl):** In the leaching tests, 55% to 70% of the Tl was leached by HF, suggesting a strong silicate affinity. In one of the three leached samples, 30% of the Tl was removed by $HNO_3$ indicating a possible iron sulphide association; in contrast, <5% of the Tl was found to have been removed by $HNO_3$ in the other two samples. This suggests Tl association with iron sulphide is only a very minor occurrence in the Greymouth coals, although relatively high Tl has been detected in iron sulfides (pyrite and marcasite) in comparison with Tl in coals by a number of other workers (e.g., Wewerka et al., 1978; Finkelman, 1981; White et al., 1989).

**Uranium (U):** The concentration of U in the E seam coal ranges from 0.13 to 0.55 ppm. The total U leached is 45% to 80%. Of the total U leached, 10% to 15% was removed by HCl, 25% to 45% was removed by HF, and 10% to 25% was removed by $HNO_3$, suggesting multiple modes of occurrence of U in the Greymouth coals.

No U-bearing mineral was detected in this study, although Finkelman (1981) reported U occurring in minerals, such as uraninite, zircon, monazite, and apatite. The U content in this coal is well below 1 ppm (with a mean U of 0.13 ppm and 0.37 ppm in the Main and E seams, respectively). However, the clay minerals extracted from raw coal contain 4 to

6.4 ppm of U, which accounts for 75% to 90% of the total U in the E seam coal, and 40% to 80% of U in the Main seam coal (**Table 4.10**). No U was detected in carbonates and pyrite examined in this study. This result suggests that U is mainly associated with clay minerals. However, the U which remained unleached (55% in 2B) is probably associated with organic matter. Many other workers (e.g. Breger et al., 1955; Gluskoter et al., 1977; Kuhn et al., 1978; and Cecil et al., 1979; Leventhal and Finkelman, 1986) also concluded from their studies that U has an organic association in coals, especially in coals with low (a few ppm) U concentration. Finkelman (1995) also concluded that most of the U in US coals appears to be organically bound, but a substantial proportion of the U in high rank coals may be associated with accessory minerals (e.g., zircons, REE phosphates).

In this study, no U was leached by ammonia acetate, suggesting no U occurs as weakly bonded cations. Although 10% to 15% of the U is HCl soluble, no U was detected in the carbonates (siderite and ankerite). One possibility is that the U removed by HCl could be present as chelated ions (Finkelman, pers. comm., 2001). The leaching results appear to indicate that U is mainly associated with clay minerals (in HF leachate) and organic matter (unleached), the phosphates admixed with the clay minerals (in $HNO_3$ leachate), and as chelated ions (in HCl leachate).

**Vanadium (V):** In the float-sink study of the E seam coal, 55% to 85% of the V is present in sink fractions (**Table 4.11**), suggesting a majority of the V is associated with mineral matter in the coal, and the balance (up to 45%) is probably associated with organic matter. Results of float-sink studies by other workers, such as Zubovic (1966), Gluskoter et al. (1977), Kuhn et al. (1978) and Miller and Given (1978), all reported V to have an organic association. In contrast, Razdorozhniy (1967) found that V was associated with inorganic matter in Russian coals. Nicholls (1968) also concluded that V was associated with inorganics and probably adsorbed onto clays. Palmer and Filby (1984) and Finkelman (1981) also found that V had an association with clays. Shearer et al. (1997) believed that the relatively high V concentrations in both peat and coal from the Waikato region (New Zealand) were controlled by the presence or absence of

inorganic sediment layers of volcanic origin (tephra). Peacor et al. (2000) in a study of an Indiana quarry, found that "V occurs in solid solution within illite-rich illite-smectite (I-S) having an average content of 1.65 wt.% V, and an overall composition of $K_{0.8}(Al_{2.8}Mg_{0.5}Fe_{0.4}V_{0.3})$ $(Si_{7.2}Al_{0.8})O_{20}(OH)_4$, analogous to the V-rich dioctahedral mica, roscoelite. The illite contains more than twice as much V as the associated kerogen".

In the leaching tests, 45% to 70% of the V was removed by HF suggesting a major silicate association, probably with illite. Furthermore, a positive correlation of V with $SiO_2$ (r = 0.7), $Al_2O_3$ (r = 0.7) and $K_2O$ (r=0.7) also suggests a clay association for V. These data indicate that V has multiple modes of occurrence.

**Tungsten (W):** In the leaching tests, 25% to 35% of the W was removed by HF, suggesting a silicate association. In sample P532A, 55% of the W was leached by HCl, indicating that some W may be associated with HCl soluble carbonates or oxides.

W in the clays of the E seam is 10 to 42 ppm, and may account for 20% to 90% of the total W in the coal. W in clays from the Main seam varies from 2 to 149 ppm, and may account for 45% of the total W in the Main seam (**Table 4.11**). No W was detected in pyrite or carbonate minerals. The balance of the W probably occurs in quartz because high W concentrations (up to 3633 ppm) were detected in quartz grains.

**Zinc (Zn):** In float-sink tests, on average 84% of the Zn was found to be retained in the sink fractions, strongly suggesting a mineral affinity (**Table 4.11**). In leaching tests, total Zn leached ranges from 80% to 100%, which also indicates a dominantly mineral association. A significant proportion (30 to 70%) of the Zn was leached by HCl suggesting a sphalerite (ZnS) and/or carbonate association; whereas 20 to 50% of the Zn was found in HF leachates, suggesting a silicate association.

Sphalerite has been reported as a primary constituent (although in small amounts) in granite (Gaines et al., 1997). Granites and granitoids were among the possible detrital

sources for the Greymouth coalfield. Zn is widely believed to occur predominantly as sphalerite (ZnS) with a small proportion of Zn occurring in pyrite (Kemezys and Taylor, 1964; Hatch et al., 1976; Finkelman, 1985; Swaine, 1990). Senior et al. (2000) also believed that Zn in two US bituminous coal samples were mostly in the form of ZnS or associated with pyrite; whereas it appears to be associated with other minerals in the other two US coals they studied.

In contrast, Zn in the clay minerals of the E seam ranges from 180 to 207 ppm, accounting for >80% of the total Zn. Siderite contains 85 ppm, and accounts for <20% of the total Zn. Clays of the Main seam have 148 to 262 ppm Zn, which accounts for almost all the Zn in the coal (**Table 4.11**). No significant amount of Zn was detected in the pyrite.

**Zirconium (Zr):** An average 79% of the Zr was found in the sink fraction of the float-sink tests, suggesting a predominantly mineral association. In the leaching tests, 45% to 75% of the total Zr was leached, with 20 to 35% removed by HF, suggesting a significant amount of Zr is associated with silicates. In addition, 5% to 30% of the Zr was leached by HCl, suggesting that some of the Zr may also be associated with carbonates. Zircon grains were observed as discrete grains with a size of sub-micron to 2 μm under SEM-EDX analysis (**Fig. 4.45**). High Zr content was always found in the intervals which are in contact with roof, floor and inter-seam inorganic parting, clearly indicating a detrital origin.

Five to 15% of the Zr was leached by $HNO_3$. This proportion of Zr is not associated with sulphides because no Zr was detected in pyrite; instead, this proportion of Zr is probably associated with phosphates because: (1) it has similar leaching behaviour to REE; (2) it may occur as an elemental replacement in xenotime[3].

[3] Xenotime is a REE-bearing mineral consisting of $YPO_4$, and it is isostructural with zircon ($ZrSiO_4$). Xenotime is commonly associated with monazite and zircon.

Clays of the E seam have 250 to 290 ppm Zr, and could account for 65% of the total Zr in the coal. Clays of the Main seam have 524 to 535 ppm Zr, and could account for 35% of the total Zr in the Main seam coal (**Table 4.11**). However, no Zr was detected in the late-stage-formed clays (samples C-TB and C-ND). No Zr was detected in carbonates and pyrite, either. Zircon was detected as inclusions in the quartz grain using the SEM-EDXA and microprobe analysis. The microprobe analysis of two Zr-bearing mineral grains shows that: (1) only Zr and Si are present in the grains, and (2) the two grains both contain minor amounts of Hf, and the molecular ratio of Si:(Zr + Hf) is consistently close to 1:2. The excess Zr content after the formation of Zircon ($ZrSiO_4$) is possibly present as $ZrO_2$ oxide. Thus, these two Zr-bearing inclusions are probably present as a mixture of zircon and $ZrO_2$ oxide. Therefore, Zr mainly occurs as zircon and is associated with syngenetic clays (probably as fine-grained zircon and as isomorphic substitution in clay), and part of the Zr probably is associated with phosphates. Zr association with inorganic matter in coal has been well documented (Gluskoter et al., 1977; Kuhn et al., 1978). Zr has also been found to occur as detrital zircon (Finkelman, 1981). Some of the Zr might possibly occur as isomorphic substitution in clays.

### 4.4.6 Organic Associated Elements

This group of elements is characterised by low total leached percentages in all leaching tests, these elements are thought to be organically bound. Generally only around 5% (which is considered to be within the analytical error) of these elements are leached by any one of these solvents, and the total leached percentage of any element components in this group is less than 15%. This suggests that these elements are not leachable by all the solvents used and indicates a probable organic association.

**Boron (B):** The total leached B (20 to 35%) is relatively low. In sample 2B, only 15% of the B was removed by ammonium acetate, 5% by HCl, 5% by HF, and 10% by $HNO_3$; whereas, in the other two samples <5% was removed by ammonium acetate, HCl, and HF, but 10% to 15% B is $HNO_3$ soluble. These results suggest that B is predominantly

associated with organic matter, and trace to minor amounts of the B are associated with weakly-bound and chelated ions, carbonates, silicates or disulphides.

Swaine (1971) concluded that B is commonly bound with organic matter in the Bowen Basin coals. Similarly Newman et al. (1997) concluded B to be organically bound in the Waikato Coal Measures. Bohor and Gluskoter (1973) found 76 to 200 ppm B in illite from Illinois coals, but this B only accounted for <5% of the total B content in these coal samples. Finkelman (1981) reported that B was mostly concentrated in float-fractions in US coals. Butler (1953) and Goodarzi and Swaine (1994) found that B content varies inversely with ash content in Canadian coals. In contrast, a positive correlation between B content and clay mineral content and a reverse relationship between B and organic carbon was noted in British Coal Measures (Eagar, 1962, Eagar and Spears, 1975). Boron is often found in New Zealand coals at levels several orders of magnitude above the mean of worldwide coals (Ross, 1957; Kear and Ross, 1961). It is widely believed that high boron coals are associated with marine water invasion. Kear and Ross (1961) argued that high B in Waikato coals were attributed to hot springs and/or seawater percolation. In this case, however, there is no evidence to suggest that a marine invasion ever influenced either the E or Main seam coals. So far no discrete B minerals have been found in coal.

In an attempt at mapping B content in high B Waikato coals using nuclear microprobe, Vickridge et al. (1990) failed to observe any hypothetical discrete calcium borate minerals nor the suspected correlation between Ca and B; they thus favoured a hypothesis of an organo-borate anion complex occurrence for B, e.g., the borate ion is possibly associated with cationic functional groups in the coal.

**Bromine (Br):** Five to 20% of the Br was removed by ammonium acetate, but less than 5% in the other three leachates. Total leached percentage of Br in all three samples is very low (15 to 20%), suggesting a dominant organic association. Br is highly mobile under a broad range of conditions, from oxidising to reducing and acid to alkaline conditions (Reimann and Caritat, 1998). Br is much more concentrated in coal than in any other rocks in the Earth's crust. No Br was detected in the clay, ankerite or pyrite

from the Greymouth coals. Only siderite contains Br (3.7 ppm, and may account for 5% of the total Br), but still only occurs in concentrations less than what is found in the coal. These results are consistent with the sequential leaching data and confirms that Br is predominantly associated with organic matter.

Gluskoter et al. (1977) and Kuhn et al. (1978) ranked Br as the most likely organic-associated-element of any element in their studies. Float-sink results also pointed to a dominant organic association (Filby et al., 1977; Finkelman, 1981) in US coals. Huggins and Huffman (1995) believed that Br is in a similar mode of occurrence of Cl (see the following discussion for Cl) in two US bituminous coals based on the preliminary bromine XAFS data. Vassilev et al. (2000) reported a characteristic Br association with illite and to a lesser extent with mica, kaolinite and Fe bearing minerals.

**Chlorine (Cl):** In the float-sink tests, an average of 36% of the Cl is present in the sink fractions, which suggests that it is mainly associated with organic matter. Cl does not correlate with ash content, $Al_2O_3$, or any other mineral-associated trace elements examined in this study, also indicating that it is not associated with mineral matter. Although Cl was detected as micron-sized crystalline halite (NaCl) under SEM-EDXA, the trace amount of halite obviously could not be a significant host for Cl.

Whilst Vassilev et al. (2000) reported Cl as an impurity in minerals and inorganic phases (such as clay minerals, mica, feldspars, polyhalite, gypsum, siderite, volcanic glass, phosphates and other carbonates and sulphates), Chou (1991) concluded that Cl occurs as chloride ions (occurring as NaCl) dissolved in pore water or as chloride ions adsorbed onto macerals in the Illinois coals. In a study examining the occurrence of chlorine in coals using K-edge X-ray absorption fine structure (XAFS) spectroscopy, Huggins and Huffman (1995) stated: "The X-ray absorption near edge structure (XANES) for coals of ranks higher than subbituminous are closely similar, regardless of chlorine content, rank and geographic origin, and indicate that there is but one major, universal mode of occurrence of chlorine in coal: chloride anions in moisture anchored to the surface of

micropores in coal macerals by organic ionic complexes, such as quaternary amine groups and alkali carboxyl complexes.... No evidence was gained for any organic chlorine in any coal...".

Because no significant amounts of Cl were found to be associated with minerals or coal ashes, thus Cl appears to be associated with macerals in the Greymouth bituminous coals.

**Cadmium (Cd):** The total leached percentage of Cd in all three samples is very low (0 to 10%). Only 5 to 10% of the Cd was found in HCl leachate, with no Cd leached by the other solvents. This suggests that Cd is predominantly associated with organic matter in the coal with minor amounts associated with chelated ions (which may account for the HCl leachable Cd).

Gluskoter and Lindahl (1973) reported that Cd predominantly occurs in sphalerite (ZnS) in Illinois coal. Finkelman (1995) reported a good correlation between Cd and Zn in US coals. However, Godbeer and Swaine (1979) found no correlation between Cd and Zn in low-Cd Australian coals. Cd was also found in pyrite (Swaine, 1990).

**Cobalt (Co):** Co concentrations in E seam coal samples range from 4.8 to 7.1 ppm. The total Co leached in three samples range from 5% to 15%. Less than 10% of the Co was removed in the HCl and HF leachates. Most of the Co (85% to 95%) remained unleached, suggesting a predominant organic affinity.

Palmer (pers. comm., 2000) reported in a study of 16 bituminous and subbituminous coals from major coal producing areas in US, that 15% to 85% of the Co remains unleached. In addition, the balance of the Co is removed in roughly equal proportions by HCl, HF and $HNO_3$, respectively, suggesting multiple modes of occurrence for Co.
In the Greymouth coal samples, Co was found to be enriched in low temperature ash (LTA). The highest Co is 739 ppm (and could account for 74% of the total Co) in one LTA sample from the Main seam, whereas the mean Co is 32 ppm in Main seam coal and ranges from 1 to 41 ppm in E seam coal (**Table 4.11**). Co in the clays of the E seam is

128 to 143 ppm and accounts for 50-90% of the total Co in the coal; Co in the clays of the Main seam is 42 to 740 ppm and accounts for 1 to 75% of total Co in the coal. Co shows a very similar behaviour to Ni in this coal (see the following discussion on Ni).

**Nickel (Ni):** In the float-sink experiments, Ni is one of few trace elements showing no clear mineral association in coal, and is even enriched in float fractions (up to 73%), indicating a major organic association.

The primary modes of occurrence of Ni in coal are far from certain due to lack of direct evidence. Although Ni was found in sulphides (galena, sphalerite, pyrite, clausthalite) and Ni-bearing sulphides [millerite (NiS), linnaeite-$(Co, Ni)_3S_4$ and ullmannite(NiSbS)] (Finkelman, 1981; White et al., 1989), Finkelman et al. (1990) reported that some exchangeable Ni (up to 55%) was associated with organic matter in 10 US coal samples. Newman (1988) speculated an organic association of Ni based on his float-sink results.

Ni in the E seam varies from 11 to 16 ppm. The total Ni leached is 10 to 30%. There is <15% of the Ni in the HCl and HF leachates. Seventy to 90% of the Ni remains unleached, clearly indicating an organic affinity in the coal.

Another very interesting observation is that high Ni content (1400 ppm) was found in the 400 °C ashes of the top interval of the E seam but not in the other intervals of the same profile. Coal samples from the top, mid and bottom intervals of the E seam were slowly heated under the 400°C ashing process. The resultant 400°C ash samples were analysed using WD-XRF. In the resultant 400°C ash samples (**Table 4.12**) from site OPC (the east margin) of the E seam, Ni was found to be as high as 1400 ppm (equivalent to 65% of the total Ni in this interval, OPC-top, with ash yield of 2.6%). In contrast Ni in ash ranges from 16 to 298 ppm in other intervals of the same profile. At this top interval of the E seam (OPC-top), calculated Ni is 36 ppm in the coal compared with the actually measured Ni of 56 ppm, indicating only 65% of Ni remained in the ash after the 400°C ashing process. Therefore, at least 35% of Ni in this top interval may have been volatilised at 400°C. Likewise, the same observation was noted in another profile, profile

637 (northwest E seam margin); the 400°C ash from the top interval of profile 637 contains 1400 ppm Ni (637-Top with ash yield of 2.8%), whereas other intervals in the same profile contain <3 to 181 ppm of Ni (**Table 4.12**). At this specific interval, 637-Top, calculated Ni is 39 ppm in the coal compared with measured 70 ppm Ni, suggesting only 56% of Ni remained in the LTA. Therefore, 44% of Ni was volatilised at 400°C. Finkelman et al. (1990) in a study of 10 US coal samples found that 10 to 30% of the Ni was volatilised at 550°C and believed that this Ni was organically associated.

In samples from the Greymouth coalfield, Ni was found to be greatly enriched in the clay fraction. Ni in clays of the E seam is 320 to 394 ppm (compared to <50 ppm in coal) and accounts for 80-85% of the total Ni in the coal (**Table 4.11**). Ni in the clays of the Main seam is 283 to 2086 ppm (<30 ppm in coal), and accounts for 45% to 55% of the total Ni in the coal. No Ni was detected in carbonates and pyrites.

Ni is usually associated with silicate minerals in igneous and sedimentary rocks, but it tends to show ambiguous behaviour in coal. Ni did not show a clear association with minerals in float-sink experiments and leaching tests, and a significant percentage (70 to 90%) of the total Ni was not leached by any of the four leachates, either. This seems to suggest that most of the Ni is probably associated with organic matter in coal.

However, clay minerals from the E and Main seams contain 80-85% and 45-55% of the total Ni, respectively. These data suggest that a majority of the Ni is associated with silicates. This is contradictory to the results of leaching tests. The possible explanation for these contradictory results is that Ni is associated with clay minerals, but only with micron or sub-micron-sized clay minerals that are intimately mixed in the coal matrix. Because of this small grain size of clays, this fraction of the clay may not be able to effectively separate from the coal matrix and may not be exposed to leaching solvents. This is further supported by the fact that no Ni was detected in the late-stage-formed clays with large grain size. This may explain why Ni shows ambiguous behaviour in both

float-sink tests (Ni-bearing clays are hiding inside coal particles) and in leaching tests (the Ni is not exposed to acid leachant).

**Selenium (Se):** Float-sink tests show that up to 64% of the Se is present in the float fractions. In the leaching tests, the total Se leached was <5% in all three samples, and it was only in $HNO_3$ leachate. The above evidence supports a dominant organic association for Se in the coal. This is consistent with the results of other studies (Finkelman et al., 1990; Dreher and Finkelman, 1992).

Se content in clays of the E seam ranges from 1.4 to 5.3 ppm, and could account for 25% to 35% of the total Se in the coal (**Table 4.11**). Se in siderite is 2.8 ppm, and could account for 10% of the Se in the coal. No Se was detected in ankerite.

Se in clays of the Main seam ranges from 6 to 15 ppm, and can account for only 10 to 30% of the total Se in the coal. Pyrite contains17 ppm Se, and can account for only 10% of the total Se in the coal. Wandless (1957), Wedepohl (1972) and Minkin et al. (1984) also reported the occurrence of Se in pyrite. In addition, Finkelman (1985) found a Se-bearing lead selenide (PbSe) in US coals. Senior et al. (2000) believed that Se is mainly associated with pyrite in the bituminous coal samples. However, in this study, a lack of correlation of Se with ash yield, any ash-forming constituents or S is further evidence supporting a predominant organic matter association for Se.

### 4.4.7 Rare Earth Elements, Th and Y

The estimated abundances (ppm) of REE in the Earth's continental crust, and in the Greymouth coal are shown in **Table 4.2**. In the float-sink tests, there are more than 70% of REE retained in the sink fractions (**Table 4.13**), indicating a clear mineral affinity in this coal. In general, REE are characterised by a significant percentage being $HNO_3$ leachable (**Table 4.13**).

In the leaching tests, REE, especially La and Ce, demonstrate high percentages removed by $HNO_3$. In sample P532A and 2A with relatively high ash yields in raw coal, 65% to 75% of the La, 75% to 80% of the Ce, 65% of the Sm, 55% of the Eu, 30% to 40% of the Tb, and 20% to 25% of the Yb were removed by $HNO_3$, respectively. Likewise, in sample 2B with a relatively low ash yield in raw coal, 40% of the La, 45% of the Ce, 45% of the Sm, 25% of the Eu, 25% Tb and 10% of the Yb were removed by $HNO_3$. Apparently, there is some difference between LREE, such as La, Ce, Sm, and HREE (e.g., Tb, Yb and Lu) in terms of their leaching behaviour. The LREE (**Table 4.13**) have a higher percentage (on average >60%) leached by $HNO_3$ than HREE (<30%). The proportion of elements removed by $HNO_3$ is generally associated with disulphides (pyrite). However, this is not the case for this coal. The reasons for this are: (1) there is little or no disulphide in the E seam coal; and (2) even though the pyrite is commonly present as a minor mineral in the Main seam, REE in the pyrite only accounts for <2% of the total REE in the coal. Moreover, the REE-bearing phosphates are soluble in $HNO_3$.

SEM-EDX observations show that the REE (especially La and Ce) are present as discrete RE phosphate grains (see **Fig. 4.46**), which are physically associated with clay minerals in most coal.

INAA determination of trace elements in minerals (**Table 4.13**) shows that a majority of the REE appear to be associated with the silicates. In the E seam, 60-90% of the LREE and 70-90% of the HREE are associated with clays, and only 1% to 18% of the LREE and 2% to 4% of the HREE are associated with carbonates. In the Main seam, 45-90% of LREE and 55-100% of HREE are associated with clays.

Seredin (1996) reported that Russian Far East coals contain high concentrations of REE (300-1000 ppm) mainly in absorbed forms (onto clays, fine-grained authigenic minerals and organic matter).

Therefore, REE mostly occur as phosphates, but the phosphates are closely admixed with clays in the coal as was observed under SEM-EDX. No doubt some REE indeed occur directly in clays by absorption mechanisms and fixation (Coppin et al., 2002).

**Thorium (Th):** In the float-sink tests, 77% of the Th is concentrated in the sink fractions (**Table 4.13**), suggesting a dominant mineral association. Moreover, in the leaching tests, 35% to 60% of the Th was removed by $HNO_3$, 5 to 10% by HCl, and 10 to 30% by HF. This indicates multiple modes of occurrence of Th in Greymouth coal. This leaching behaviour is very similar to the REE, suggesting that Th is mainly associated with phosphates and clays as discussed previously. Finkelman (1981) and Palmer and Filby (1984) also found that Th is associated with monazite, xenotime and zircon.

Five to 10% of the Th was found in the HCl leachate, suggesting a minor carbonate or phosphate association for Th. Furthermore, Th concentration in both carbonates (siderite and ankerite, 0 to 0.3 ppm) and pyrite (0.4 ppm) is lower than coal, supporting that carbonate and pyrite are only minor hosts for Th. Th was observed in quartz grains (**Fig. 4.47**) as well as in clays under SEM-EDXA.

Th in the Greymouth coals ranges from 0.1 to a few ppm (mostly <1 ppm). But Th is 17 to 24 ppm in the clays of the E seam, and could account for 80% of the total Th in the coal; likewise, Th is 19 to 27 ppm in the clays of the Main seam, and could account for 35% to 85% of the total Th. In contrast, Th in the pyrite and carbonates is 0.4 ppm and 0.3 ppm, respectively, and could only account for <1% of the total Th.

Th in pyrite (0.4 ppm) is in much the same concentration as in the raw coal, but dramatically lower than the 17 to 27 ppm found in the clays. However, Th demonstrates a strong correlation with LREE ($r = 0.9$) and HREE ($r = 0.8$), in addition to a good correlation with $Al_2O_3$ ($r = 0.8$) and $P_2O_5$ ($r = 0.6$) (**Fig. 4.53**). This suggests that some Th is probably associated with phosphates (monazite, xenotime), and this result is also supported by the leaching results. Thus the majority of leached Th (35% to 60%) by

$HNO_3$ is not hosted in pyrite, but by phosphates; in fact, very little sulphide was found in samples from the E seam coal. Therefore, Th is mostly associated with clays and phosphates which are physically admixed with the clays in the Greymouth coals.

**Yttrium (Y):** Y is geochemically closely related to rare earth element-bearing phosphates. In float-sink experiment, 75 to 95% of the Y was found to be concentrated in the sink fractions (**Table 4.13**), clearly indicating an inorganic affinity. In the leaching tests, 30 to 55% of the Y was leached by HCl, 10 to 35% by HF and 15% to 50% by $HNO_3$, indicating a multiple modes of occurrence (carbonate, silicate and phosphate association, respectively) for Y in the Greymouth coal. Some plants [e.g., hickory (Carya)] can accumulate Y which may replace Ca in its biological function (Reimann and Caritat, 1998). Y is probably associated with REE-bearing phosphates (xenotime, apatite and monazite) and clays. Finkelman (1981) found that Y occurred predominantly as finely-xenotime grains dispersed in the US bituminous coals he studied.

## 4.5 Modes of Occurrence of Pb and Cr

Both Pb and Cr in the Greymouth coals may in fact occur within the mineral crocoite. However, based on their concentrations in both the E and Main seams and their remarkable atomic mass difference [Pb (207) and Cr (52)], only around 15% of the total Cr is needed to meet the molecular 1:1 demand of forming mineral crocoite ($PbCrO_4$) if all Pb in the coal occurs in crocoite. Most of the Cr is associated with illite as previously discussed in **Section 4.4.5**.

Crocoite was found in raw coal samples within the lower part of the Main seam core samples (see **Fig. 3.12** and Li et al., 1999b) as well as in the fresh E seam underground coal sample (see **Fig. 3.13**). The coal has generally low abundances of almost all trace elements on a whole coal basis, but locally high concentrations of some elements (e.g., Pb and Cr). X-ray diffraction (XRD) and bulk chemical data from a SEM equipped with an energy dispersive X-ray analyser (EDXA) have confirmed the identity of the mineral

crocoite. This is apparently the first time that crocoite has been reported in coal. The unusual and hence interesting occurrence of Pb is quite different from what appears in the literature on the modes of occurrence of Pb in other coals (see Swaine, 1990; Finkelman, 1980).

During microscopy examination of LTA samples, bright orange-red grains were observed. However, one of the major concerns was whether this unknown mineral was present in coal or was an artifact of the LTA process. One possibility was that the unknown mineral was a Fe-oxide, perhaps as the oxidation product of pyrite or another Fe-bearing phase. To address this concern, polished blocks of raw coal samples were examined. Several examples of this mineral were found in two samples in the lower split of the Main seam in drillhole 755. Interestingly, recently exposed fresh coal samples (underground) from a stratigraphically similar seam (E seam) were also found to contain these types of crystals. Sizes of the crystals generally ranged from <0.1 mm to 2 mm, they possessed an adamantine to vitreous lustre, and were tabular in shape (**Fig. 3.12**); the colour tended to be bright orange-to-red sometimes coated with a white, very thin film of another phase [possibly cerussite ($PbCO_3$)]. The handpicked specimen grains of this mineral were then subjected to further elemental and mineralogical analysis.

Crocoite usually occurs only in the oxidised zone of lead mineral deposits. Gaines et al. (1997) believed that crocoite, as a secondary mineral found in the oxidised zone of lead deposits, most likely formed later than anglesite, but usually earlier than cerussite. The occurrence of this mineral in both the Main and E seam coals implies that the deposit may have been exposed to an oxidising environment at some stage, most likely after coalification.

### 4.5.1 Elemental Chemistry

The selected elemental profiles of Pb, Cr, S, Fe and ash are given in **Figure 4.55**. It was noted that the abundance of Pb and Cr increase dramatically at the lower part of the split.

To identify the bright orange-red mineral, elemental composition and crystal structure data are needed. Thus, a few grains of this mineral were mounted and examined under SEM-EDXA to determine the bulk elemental composition (**Fig. 4.56**). The semi-quantitative results of SEM-EDXA are given in **Table 4.14**. The microprobe analysis results are given in **Table 4.15**. Both the SEM-EDXA and microprobe analyses show that only Pb and Cr are present. After multiple analyses on six different grains, both the semi-quantitative results of SEM-EDXA and quantitative microprobe results consistently demonstrated that the unknown mineral is a Pb-Cr compound with molecular Pb/Cr ratio of approximately 1:1, and that it is probably an oxide.

In the float-sink tests, on average 56% (with a range of 22 to 82%) of the Pb concentrated in the sink fractions, indicating a dominant mineral association. In the leaching tests, 25 to 55% of the Pb was removed by HCl, 20 to 30% by HF and 10 to 25% by $HNO_3$, indicating complex modes of occurrence of Pb in the coal.

Interestingly, a simple calculation reveals that both the dissolved Pb and Cr in the HCl leachates consistently show a molecular Pb:Cr ratio of approximately 1:1 in all three samples. This observation reflects the dissolution of the mineral crocoite ($PbCrO_4$) in HCl leaching process and the chemical reaction involved is:

$$2PbCrO_4 + 2HCl \longrightarrow 2Pb^{2+} + Cr_2O_7^{2-} + 2Cl^- + H_2O \qquad (2)$$

Due to the low Pb concentration (27 to 184 ppb) in the HCl leachates, the resultant $Pb^{2+}$ is unlikely to be precipitated (as $PbCl_2$) in HCl solution. Thus, this significant amount (up to 55%) of Pb leached by HCl is associated with $PbCrO_4$, not carbonate ($PbCO_3$) or galena (PbS). Although galena (PbS) was not found in the mineralogical study, a small amount of Pb occurring as galena cannot be completely ruled out because: (1) on average 15% of the Pb was leached by $HNO_3$ which indicates a possible sulphide (PbS) association, (2) PbS is unlikely to be dissolved in the previous HCl and HF leaching steps, but it is $HNO_3$ soluble. However, PbS can only be a minor mode of occurrence for Pb if any exists. The chemical reaction involved is:

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 3S + 4H_2O + 2NO \qquad (3)$$

Therefore, Pb is predominantly associated with crocoite, but minor amounts of the Pb associated with the silicate and/or galena (PbS) cannot be ruled out.

### *4.5.2* X-ray Diffraction Results

The powder XRD study on the bulk LTA showed that the major minerals were clays (kaolinite, illite and mix-layered smectite) and quartz, with a small amount of sulphides (primarily pyrite), carbonates (calcite, siderite, ankerite), and traces of sulphates (gypsum), salt (halite, sylvite) and other silicates (Li et al., 1999a). For this study, an XRD pattern was obtained on a single crystal of the Pb-Cr mineral. The *d* and intensity (*I/I1*) values of both this mineral and a JCPDS (Joint Committee on Powder Diffraction Standards) crocoite standard (Smith et al., 1967) are given in **Table 4.16**. The *d* values are the perpendicular distance between different reflecting planes of the crystal structure. Therefore, the *d* value is the spacing of the planes, which produce the given reflection. Both the *d* values and intensities (*I/I1*) of the Pb-Cr mineral show very good agreement with those of the crocoite JCPDS data (**Table 4.16**). The difference between correspondent *d* values of the sample data and standard data is well below the 2% experimental error that would normally be encountered (Smith et al., 1964). Therefore, the Pb-Cr mineral in the coal is confirmed as crocoite.

### 4.5.3 Geochemistry

Crocoite has not been reported as occurring in coal. In vertical profiles of the Main seam, Pb and Cr vary concomitantly (**Fig. 4.55**). Ash yield, Fe and S contents also vary together, but their variation is quite dissimilar from that of Pb and Cr. The high correlation between Pb and Cr (r = 0.89) and lack of correlation between Pb and S (r = -0.228) is consistent with the conclusion of Pb occurring as crocoite. Furthermore, Pb and Cr do not correlate well with ash content (r = 0.45 and 0.65, respectively). This suggests

that Pb and Cr are not directly derived from the same source as much of the other mineral matter. Moreover, the euhedrally tabular crystal with sharp angle morphology of crocoite grains (**Fig. 3.12**) suggests that they have not been transported far, if at all, and are definitely not detrital in origin.

The occurrence of crocoite in the Greymouth coals is apparently the first noted and reported for any coals. Crocoite occurrence contributes a significant portion of the Pb content to Greymouth coals, which is not what has been observed elsewhere. Finkelman (1981, 1995) and Swaine (1990) concluded that sulphides (e.g. PbS) are the major mode of occurrence for Pb in coal. However, this is not the case in the Greymouth coals, because (1) the only Pb-bearing mineral found is crocoite; no PbS was found in the Greymouth coals; (2) Pb and Cr co-vary and display good correlation (r = 0.89), but no clear correlations between the Pb and S exist. All this suggests that PbS is not a major host for Pb.

Crocoite ($PbCrO_4$) is known as a secondary mineral occurring in the oxidised zones of lead deposits. However, there are no lead deposits in the Greymouth coalfield. A hypothesis is that the numerous fault systems that occur within the coalfield may be a source pathway for the Pb. It is possible that Pb has been secondarily leached from either basement or adjacent sedimentary rocks and then incorporated/fixed by organic matter and finally re-deposited within the coal. Under any emplacement mechanism, though, the presence of crocoite in the Greymouth coals represents an unusual and very interesting mineralogical occurrence.

## 4.6 Discussion

### 4.6.1 The Significance of Vertical and Lateral Variations of Trace Elements

Most trace elements show a general vertical trend of relatively high concentrations in the base of the seam. Sometimes high concentrations occur in the top layer as well. This

uniform distribution trend is probably related to leaching processes in the peat and post-burial stages, which have been discussed in Chapter 3. Leaching processes probably account for the in-seam mobilization of trace elements; whereas some of trace elements may have been moved out of the coal sequence, the rest have been retained in the basal part of the seam. However, a few trace elements are also enriched within the central parts of the seams. For example, Pb at certain horizons in both the Main and E seams is found at high concentrations, up to 120 ppm (Li et al., 2001c).

Another significant vertical trend is that most trace elements (especially HAPs) are dramatically elevated in two peaks near the bottom of both seams, as observed in the locations OPC, 283 and 2A/B of E seam as well as DH 703 and DH 755 of the Main seam. These similar variation trends over a wide area across the basin may be controlled by the similar depositional events (such as flooding or detrital invasion events in the peat or after burial stages) across both the E and Main beds. This trend may be useful for seam correlation and coal quality management as well as HAPs prediction of target coal production.

Laterally, a general trend of trace element variation was also noticed. The concentration of most trace elements increases from the centre of the E seam towards the basin margins. This is especially true from the basin centre toward the NW and south of the E seam, which may have been in the direction of the original source of most of the inorganic matter.

### 4.6.2 The Significance of Modes of Occurrence

Knowing the modes of occurrence of environmentally-sensitive elements (especially HAPs), can help us not only understand the possible mobility of toxic elements and predict any potentially undesirable environmental impacts associated with the target elements (Li et al., 2001c), but also provide the knowledge to mitigate those problems if they arise.

By combining both direct evidence (SEM-EDX, microprobe analysis, trace element content in minerals) and indirect evidence (float-sink experiments and sequential leaching tests), this study has been able to determine modes of occurrence of trace elements and to quantify different modes of occurrence for most trace elements. The modes of occurrence for individual elements are summarized in **Table 4.17**. The results show that most trace elements are dominantly associated with minerals (mainly clays) in the coal; although, some trace elements (B, Br, Cd, Cl, Co, Ni and Se) were found to be organically bound or as sub-micron-sized minerals intimately admixed in the organic matrix. Most trace elements, especially Ba, Cr, Cs, F, LREE, HREE, Rb, Sc, Th and U are well-correlated with ash content, $Al_2O_3$ and $K_2O$ in coal due to their association with mineral matter; in contrast, a few other trace elements (As, Br, Cl, Co, Ni, S and Se) demonstrate no correlation with ash content, $Al_2O_3$ or $K_2O$ in coal due to their organic association. There are four major findings of trace elements in this study, these are:

(1) The first report of crocoite ($PbCrO_4$) in coal as a major host for Pb and $Cr^{6+}$(which is the most toxic form in Cr compounds), although most Cr (as $Cr^{3+}$) is present in the clays. The presence of crocoite correlates with the intervals with locally high Pb concentration in both the Main and E seams. Due to this unusual occurrence and potential toxicity of crocoite, both Pb and Cr may pose potential environmental concerns if they are released to the surface or into ground waters in significant amounts. Therefore, it is prudent to take some measures to monitor the release of these two elements ($Cr^{6+}$ and Pb) when mining those intervals.

(2) In contrast to the "macerals association" of Cr in the US bituminous coals (Huggins et al., 2000), Cr was found to occur mainly in illite in addition to the unusual occurrence of crocoite in the Greymouth coals.

(3) In contrast to a dominant sulphide association for As, Hg, Sb and Zn in other bituminous coals reported in the literature, these elements were all found to be predominantly associated with clay minerals with only minor association with pyrite in this coal.

(4) In addition to the uncertain "organic association" of Co and Ni reported in other coals, a significant portion of Co and Ni were found to be mainly associated with sub-micron-sized clays, which are intimately dispersed throughout the organic matrix.

These conclusions suggest that the trace element contents of Greymouth coals warrant further study in terms of monitoring the amount of environmentally-sensitive trace elements released to surrounding environments (e.g. surface and ground waters, soils) during coal mining. High concentrations of some toxic metals released from other areas of coal-mining operations in New Zealand have been found, with elevated levels of Ni, Pb and As (Leon and Anstiss, 2002). These levels are well above the standards for drinking water.

### 4.6.3 The Significance of Rare Earth Elements (REE)

Trace element concentrations in sediments result from the competing influences of the provenance, weathering, diagenesis, sediment sorting and the aqueous geochemistry of the individual sediments. After all these processes, the highest concentrations of trace elements are found in the clay-rich fractions. REE are the most useful elements for determining sedimentary provenance because REE are: (1) in such low concentrations in sea and river water, (2) less affected by the influence of weathering, diagenesis and metamorphism, and (3) transported exclusively in the detrital component of a sediment and therefore reflect the chemistry of the source. Therefore, REE are widely used as an important tool to identify the provenance of clastic sediment as well as igneous rocks (Fleet, 1984; McLennan, 1989). In an important study on the effect of sedimentary sorting on REE concentrations, Cullers et al. (1987) found that the REE pattern of the source was most faithfully represented in the clay-sized fractions of the sediment, and they concluded that "If REE content of source rocks is preserved in fine-fractions of mudstones or sandstones during transportation and diagenesis, REE distributions could become an important tool for the determination of locally derived sources...". Therefore, many workers have used the REE patterns of the clay mineral portion of a sediment or

clay-rich sediments to establish the sedimentary processes and to identify provenance. The presence of quartz and carbonate have a diluting effect on REE concentrations.

In the attempt to determine the source of the inorganic constituents of the Greymouth coals, chondrite normalized REE patterns of coals, inorganic partings, and clay minerals of the Greymouth coals as well as those of basement rocks (Greenland Group, granitoids) in this region were determined. It was found the REE patterns of whole coals, inorganic partings and clay minerals of the Greymouth coals are very similar to REE patterns of basement rocks in the Greymouth coalfield. This finding strongly supports the view that the inorganic constituents of the Greymouth coals are indeed sourced from the basement rocks of this region.

The REE patterns of whole coal, inorganic partings, and the mineral matter extracted from LTA and coal are given in **Figures 4.57 to 4.65**. The REE pattern of basement rocks (Greenland Group, granitoid, roof rocks) close to the Greymouth coalfield are given in **Figures 4.66 to 4.68**. These REE patterns have the following characteristics:

(1) all REE patterns of both the E and Main seam coals are very similar to each other in shape, and they are also very similar to the REE patterns of LTA ash and clay minerals extracted from this coal.

(2) all REE patterns of this coal and clay minerals (**Figs. 4.57 to 4.65**) derived from this coal are found to be very similar to the basement rocks (Greenland Group rocks, granite, granitoids, etc.) in this region (**Figs. 4.66 to 4.68**) surrounding the Greymouth coal basin.

(3) all REE patterns reflect clear positive correlations with ash yields of the coal; the higher the ash yield in the sample, the higher the REE contents in the coal. However, the normalised REE patterns are always similar to each other regardless of the ash yield. Finkelman (1980) noted a similar relationship in lignites in the U.S. Gulf Coast.

(4) all REE patterns are enriched in LREE ($La_N/Yb_N$ = 0.9 to 66.6) but with flat HREE ($Gd_N/Yb_N$ = 0 to 9.2).

These characteristics strongly suggest that (1) the Main and E seam coals generally have derived their inorganic constituents from the same source, and (2) the strong similarity between the REE patterns of the coal samples and regional basement rocks reflect the strong influence of these basement rocks in terms of detrital provenance. The sedimentary data (Newman and Newman, 1992) and palynological features (Ward, 1997) also support this conclusion. Moreover, the ash contours (see Chapter 3 and **Fig. 3.5**) of the Main seam identified two high ash zones: one sits on the NW margin of the Main seam, where there was an area of high relief in the paleotopography that supplied sediments from erosion of the basement rocks to the coal basin. The other high ash zone was along the east margin of the Main seam, where it was believed (Bowman, 1982, 1984; Newman and Newman, 1992) a paleochannel existed. This presumably served as a ready source of inorganics during seasonal flooding.

## 4.7 Conclusions

Vertical and lateral variation trends of trace elements in Greymouth coals have been identified. Knowledge of trace element distribution in coal seams may be useful in seam correlation, as well as identification and prediction of any potentially undesirable horizons in coal seams with high concentrations of environmentally sensitive trace elements. These are important factors in the planning and design of the mining application and the management of coal quality.

Due to the low concentration for all HAPs in the Greymouth coals, physical cleaning would be generally unnecessary.

The modes of occurrence of individual elements are summarised in **Table 4.17**. In summary, the modes of occurrence of trace elements in Greymouth coals can be

categorised into four different groups based on the mineralogical study, float-sink experiments and sequential acid leaching tests results.

Group I is associated predominantly with silicate minerals (clays). This group includes some HAPs (As, Be, Cr, Hg, Sb and U), traditional silicate-associated elements (Rb, Sr, Sc, V, Li, W, Zr) and other elements Ba, Cs, Hf, Mo, Sn, Tl and Zn.

Group II is mainly organic-associated elements, including B, Br, Cd, Cl, Co, Ni and Se.

Group III has a major phosphate association including REE, Th, Y, P and Ca.

Group IV is a crocoite occurrence for Pb and some Cr.

In addition, major elements including Mg, Mn, Fe and part of Ca were found to be mainly associated with carbonates such as siderite, ankerite and calcite. This is especially true for E seam coal in the Strongman area. In contrast, most Fe occurs as pyrite in the Main seam. Ti was found to occur as $TiO_2$ but mainly associated with clays in the coal.

# Chapter 5

# Chapter 5 Combustion Behaviour of Elements

## 5.1 Introduction

### 5.1.1 Aims of Combustion Tests

With increasing awareness of the environmental impact of coal combustion and stringent regulations on some potentially hazardous air pollutants' (HAPs) emissions in developed countries, the behaviour of trace elements during mining and subsequent utilisation has attracted a great deal of interest. The US Clean Air Act Amendments of 1990 (U.S. Statutes at Large, 1990) specifically identified As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se and U as potential HAPs. Some coals with a high abundance of potentially toxic trace elements, especially those potential HAPs, may become less useable or unusable in the near future, if stringent regulations on HAPs emissions have to be met. This could lead to mine closures or require the introduction of coal cleaning or blending technology to produce beneficiated coal products. Some workers have undertaken studies looking at trace element occurrence in coal (Finkelman, 1981, Swaine, 1990), trace element partitioning in combustion ashes (Clemens et al., 2000), and the mobility of those trace elements in coal and combustion ashes (Querol et al., 1996, Gentzis and Goodarzi, 1999).

However, the behaviour of trace elements can vary significantly between different coal beds simply because they have different modes of occurrence or because they are used under different combustion conditions. There is few geochemical rules that apply universally to all coals because of the complexity of trace element occurrence and behaviour upon combustion. Therefore, this study is designed specifically to investigate the Greymouth Cretaceous coals and their behaviour of selected trace elements during combustion. The study also aims to identify the mineralogical transformations occurring within the combustion chamber in order to gain a better understanding of the factors influencing the partitioning behaviour of those trace elements. This understanding of trace element behaviour allows us to assess their environmental impact, identify any undesirable impacts and avoid or mitigate these potential problems.

In order to understand trace element behaviour during combustion, combustion tests were performed on three seam composite samples. The major and trace elements from sub-samples of feed coal, bottom ash, fly ash and flue gas have been analysed by inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence (XRF) and scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) techniques. A float-sink experiment was also employed to determine the association of trace elements; INAA was also employed to determine trace element content in float and sink fractions of fly ash as well as three major phases in the bottom ash. Mass balance and partitioning of major and trace elements have been studied to determine the fate of trace elements after combustion. Finally, the environmental significance of some trace elements in combustion ash, especially HAPs are discussed.

### 5.1.2 Combustion Conditions, Monitoring and Combustion Products Collection

Coal samples were combusted in an underfed stoker unit with approximately 50 kW capacity. The rig was thoroughly cleaned before each combustion run. The rig consisted of a small (200 mm diameter) retort with a ceramic hearth inside a steel furnace chamber (**Fig. 5.1**). The size of the coal ranged from 12 to 30mm. No overfire air was used. Stack velocities of between 3.7 to 3.8 m/second corresponding to stack volumetric flows of 65 to 68 cubic metres per hour were obtained and stack-sampling temperatures were between 205 to 209°C. The flame temperature in the firebox was between 1100°C to 1250°C. The furnace exit gases passed over a convective tube bank, which controlled the stack sampling temperature. Particulate matter was removed by a high efficiency cyclone. Inlet air flow and stack gas flow were measured using orifice plates, and thermocouples were used for temperature measurement.

In order to ensure reasonable combustion, firebox conditions were maintained throughout each combustion run. The flue gas (FG) was monitored for oxygen, carbon dioxide, carbon monoxide and methane content by withdrawing gas and passing it through a drying tower and into an on-line gas chromatography gas analyser.

After each run, samples of bottom ash and fly ash (FA, also commonly referred as cyclone ash) were recovered and weighed. The bottom ash (BA) was further divided into little bottom ash (LBA) (deemed to be non-slagging ash and capable of passing through a 1.7 mm sieve opening) and big bottom ash (BBA) that is retained on a 1.7mm sieve opening and deemed to be slag. The ashes were then analysed for major elements by XRF and for trace elements by ICP-MS as described elsewhere (Clemens et al., 2000, Li et al., 2001a, 2001b).

## 5.2 The Characterisation of Feed Coal

As indicated above, three combustion runs were performed on three underground coal samples taken from Strongman E seam. One of the three samples (P532A) was taken from the high ash zone, NW of the E seam workings, whereas the other two samples (2A and 2B) were taken from the low ash zone, at the centre of the E seam mining area (see **Fig. 1.5**). The coal quality data of these three combustion samples are shown in **Table 5.1**.

### 5.2.1 Mineralogy of Feed Coal

The mineralogy of the three combustion samples is generally similar to that of all other ply samples taken from this area, and has been discussed in detail in Chapter 3 and also addressed in other papers (Li et al., 1999a, 2001a). Only a brief description of mineralogy will be given here.

The major minerals found in the feed coal were clays (mainly kaolinite, illite, and minor smectite), quartz, and carbonates (mainly siderite, ankerite and calcite, etc.). The minor minerals include sulphides (pyrite, marcasite) and phosphates (apatite, crandallite, monazite, etc), with trace amounts of sulphates (gypsum), oxides (anatase $TiO_2$, hematite, magnetite, etc.), chlorides (NaCl, KCl), zircon and other silicates (biotite). Crocoite ($PbCrO_4$) was also found in both the Main and E seams (Li et al., 2001b).

### 5.2.2 Major Elemental Geochemistry of Feed Coal

The major element geochemistry has also been discussed in Chapter 3 and elsewhere (Li et al., 2001a); therefore, only a brief description will be given here. Major elements were categorised into two groups. Group I includes $SiO_2$, $Al_2O_3$, $K_2O$, $TiO_2$, MnO, MgO, CaO, and $P_2O_5$. $SiO_2$ associated with clay minerals and quartz, which is the controlling factor for the ash content of the coal. $SiO_2$, $Al_2O_3$, $K_2O$, $TiO_2$ are associated with clays, whereas $Fe_2O_3$, MnO, MgO are associated with carbonates. $P_2O_5$ and CaO are associated with phosphates. Group II includes S and $Na_2O$. A majority of S is associated with organic matter in the coal although some S is associated with pyrite. $Na_2O$ is associated with silicate and salt.

### 5.2.3 Float-Sink Behaviour of Trace Elements in Feed Coal

All three E seam samples (from Strongman No. 2 Mine) used in the combustion testing were also subjected to the float-sink test in order to determine whether trace elements are associated with organic matter (e.g., enriched in float fraction) or with mineral matter (e.g., enriched in sink fraction). After float-sink experiments, the trace element concentrations in the float and sink fractions for the three samples are given in **Figure 5.2;** the weight percentages in the float and sink fractions are given in **Figure 4.50**. Rb, Sr, Ba, Y, Cr, Zn, Zr, Th, and to a lesser extent, F and REE, are associate with mineral matter (i.e. they are enriched in the sink fraction); in contrast, Cl, S, Se, As and Ni are associate with organic matter (enriched in the float fraction), especially for the low ash yield sample 2B. This is not an unexpected observation because all those elements with mineral matter association are typically silicate-prone elements. These elements tend to be present in silicates (kaolinite and muscovite) either as tiny discrete mineral inclusions or as an elemental replacement in the silicate crystal structure.

### 5.2.4 SEM-EDXA Observation of Trace Elements in Coal

Many trace elements are present in Greymouth coals at low levels compared with US coals with similar rank (see **Table 4.2**). Most were present at or below the detection limit

of SEM-EDXA, and therefore direct identification of most trace elements was not always possible. Of the elements that were detected by SEM-EDXA, Pb and Cr were found occurring as the mineral crocoite ($PbCrO_4$ see **Figs. 3.12 to 3.13**); Zr was detected in zircon grains (see **Fig. 4.45**); Hf was detected in zircon grain under microprobe analysis in this study. La and Ce in phosphates (e.g. monazite) (**Figs. 4.46a and 4.46b**) and Th, Cr, Ti in clays (**Fig. 4.48 a and b**).

### 5.2.5 Leaching Behaviour of Trace Elements in Coal

The leaching behaviour of trace elements in the feed coal was discussed in Chapter 4 and detailed information regarding leaching results is contained in that Chapter. **Table 5.2** gives leached percentages for all elements in each of the sequential leaching tests.

The total percentages of leached B, Cd, Br, Se, Ni and Co are low (5% to 35%) in the sequential leaching tests, with no more than 15% being removed by any one of the acids. This suggests that these trace elements have a close association with organic matter in coal, either loosely bound to the organic matter or as sub-micrometre-sized mineral grains intimately dispersed in the organic material. In contrast, a significant proportion (30% to 65%) of the total Cr, Sb, Zr, Rb, Sr, V and Ba are removed by HF. This suggests association with silicates. A substantial proportion of Zn (30-70%), Y (30-55%) and Pb (25-55%) have been leached by HCl, suggesting a sphalerite (ZnS) occurrence for Zn, a Y-bearing phosphate association for Y and a crocoite occurrence for Pb.

## 5.3 Coal Combustion Products

The weights and corresponding percentages of individual combustion products are given in **Table 5.3**. It is noted that feed coal with the lowest ash (2B) has the highest ash content in the fly ash fraction (6.7%). This can be attributed to the fact that in sample 2B, the ash-forming minerals are predominantly micron and submicron sized clays intimately dispersed in the coal matrix. When the coal burns, more submicron-sized particulates

enter the flue gas down stream of the combustor and are recovered from the fly ash fraction.

## 5.4 Combustion Ash Chemistry and Mineralogy

### 5.4.1 Chemistry of Major and Minor Elements in Combustion Ashes

Major element analyses are given in **Table 5.4** and illustrated in **Figure 5.3**. Generally speaking samples 2B and P532A have similar compositions for most major elements in all three combustion ash types (BBA, LBA, FA). $Na_2O$ in sample 2B is higher in all three ash types, as is $SO_3$ in the fly ash. In contrast, sample 2A is distinguished by having significantly higher $SiO_2$ and lower $Fe_2O_3$ and MnO concentrations (**Fig. 5.3**).

Major element partitioning has the following characteristics:

(1) Si and Al predominantly partitioned into aluminosilicate glass, which often contains minor amounts of K, Ti, Ca, Mg, S, and in some cases trace amounts of Na and Cl.

(2) Fe mainly occurred as Fe-bearing spinel group minerals [$(A, B)O_3$ and $AB_2O_4$, where A= $Fe^{2+}$, $Mg^{2+}$, $Ca^{2+}$; B = $Fe^{3+}$]. Fe was also seen in some cases as Fe-S-O glass, possibly as Fe-sulfate, $Fe_2(SO_4)_3$.

(3) Ti and Fe were detected as discrete inclusion grains (possibly oxides) encapsulated inside larger quartz or Si-Al glass. Some Ca and Mg were incorporated within aluminosilicate glass. Some Ca, Mg, and Mn were also associated with Fe-bearing spinel minerals. Ca was also present as small (<1 μm in size) CaO crystals.

(4) It is widely accepted that S is mainly presents as $SO_x$ (mainly $SO_2$) and is emitted into the atmosphere from flue gas. This is especially true for those coals with dominantly organic sulphur, such as the Greymouth coals used in this study. Some $SO_2$ may interact with other elements adsorbed on fly ash particles to form sulphates. Sulphate and phosphate were also occasionally detected under SEM-EDXA as small discrete grains, such as $BaSO_4$ (see **Fig 5.4**). Phosphorus is

apparently associated with phosphates, such as apatite $Ca_5(F, Cl, OH)(PO_4)_3$, in particles less than 1 μm in size.

### 5.4.2 Mineralogy of Bottom Ash and Fly Ash

The mineralogical composition of the bottom ash and fly ash obtained from the three Strongman combustion runs are quartz, Si-Al silicates, iron spinel oxides as the major phases. The detail of these phases are given below.

#### 5.4.2.1 Bottom Ash Mineralogy

The main phases of minerals in bottom ash are quartz, amorphous aluminosilicate glass, mullite, Fe-bearing spinel group oxides (mainly haematite and magnetite), incompletely burned siderite residue, and minor amounts of submicron-sized CaO, sulphate ($BaSO_4$), phosphates [$Ca_5$ (F, Cl, OH) $(PO_4)_3$, (La, Ce, Y, Th)$PO_4$], and chlorides (NaCl, KCl). However, it is often found that K, Ca, Fe, Mg, Mn, and to a lesser extent, Na, Cl, are encapsulated within an aluminosilicate glass matrix during combustion.

In addition to the associations listed above, SEM-EDXA observation and analysis revealed three glass phases. These were:

(1) a Si-Al-O rich phase with minor amounts of K, Ca, Fe, Mg, Na,

(2) an Fe-O rich phase with minor amounts of Mg, Mn, and

(3) an Fe-Ca-Mg-O rich phase.

While the first group of glass (Si-Al-O rich phase) is the result of combustion of silicate minerals (clays) in the feed coal, the other two groups of glass are related to the siderite and other Fe-Ca-bearing minerals (calcite, ankerite and Fe-oxides).

#### 5.4.2.2 Fly Ash Mineralogy and Major Element Partitioning

The mineral composition of fly ash is very similar to that of bottom ash, although the proportion of each phase (mineral or glass) differs. The main phases present in fly ash are

quartz, amorphous aluminosilicate glass, Fe-bearing spinel group minerals (haematite and magnetite), with minor amounts of sulphates ($BaSO_4$), salts ($Na_{1-x}$, $K_x$)Cl, and copper oxide [CuO, ($Fe_x$, $Cu_{1-x}$)O].

### 5.4.3 Mineralogical Transformation During Combustion

In order to identify the mineralogical decomposition and transformations taking place during coal combustion, an experimental approach was taken in an attempt to simulate the different stages of the coal combustion process. The approach is to heat the low temperature ash (LTA, generated from a low temperature asher) in a furnace under oxidizing and reducing conditions to 400°C, 800°C and 1000°C. These are temperatures which the mineral matter present in the coal passes through as it is introduced into the firebox of the combustor . A subset of resultant ash samples was then collected for XRD examination in order to determine the mineral phase changes that occurred. The mineral phase transformations are given in **Table 5.5**.

#### 5.4.3.1 Under Oxidizing Conditions

On heating from ambient to 400°C, no obvious mineralogical transformation was observed. Major minerals are quartz, kaolinite, siderite and muscovite in all three samples P532A, 2A and 2B; there is a trace amount of ankerite present in the LTA and 400°C sample of 2B. All these minerals undergo no decomposition reaction at this stage. The x-ray diffractogram of LTA ash are show in **Fig. 5.5** and the XRD trace is the same as LTA after heating to 400°C.

On further heating from 400°C to 800°C, some obvious mineral decomposition begins to occur. Siderite and ankerite are oxidised to haematite and magnetite respectively. Any pyrite is also oxisidied to haematite (Srinivasachar et al., 1990a). Illite dehydroxylation occurs between 600-700°C under slow heating (Srinivasachar et al., 1990b). Muscovite transformed into dehydroxylated muscovite and kaolinite decomposed into amorphous

dehydroxylated kaolinite phase. Quartz remained unchanged. Quartz and haematite are the major mineral phases remaining at 800°C (**Fig. 5.6**).

After the 1000°C treatment, most dehydroxylated muscovite had been consumed and formed amorphous aluminosilicate glass, although a small amount of dehydroxylated muscovite may still be retained. Mullite (usually formed at above 1200°C) is probably being crystallized at this stage from the amorphous dehydroxylated kaolinite. This process is probably occurring in all samples, but is evident only in sample 2B. Quartz and haematite are the major mineral phases with Al-Si glass. There is a trace amount of three unidentified phases present after heating to 1000°C (**Fig. 5.7**).

#### 5.4.3.2 Under Reducing Conditions

On heating from ambient to 400°C, XRD shows the phase composition of the ash samples are generally unchanged. The major minerals are quartz, kaolinite, siderite and muscovite in all three samples. Sample 2B has trace amounts of ankerite. After 400°C treatment, a trace of metallic iron was detected in two of the three samples. The metallic iron is apparently reduced from siderite (and possibly ankerite if available). Sample 2B contains slightly more of this metallic iron than sample P532A.

Further heating from 400°C to 800°C, leads to increased amounts of metallic iron being generated from siderite and ankerite by carbonate reduction. Increasingly from this process, metallic iron becomes one of the two major phases. Interestingly minor amounts of magnetite were detected only in sample 2A. This sample has the lowest Fe content in ash constituents of the three samples. Clay minerals (mainly kaolinite) and muscovite have dehydroxylated. The mica probably has been decomposed and formed dehydroxylated muscovite, whereas dehydroxylated kaolinite is amorphous and subsequently formed aluminosilicate glass at a higher temperature. Four further unidentified phases were detected in two of the three samples (**Fig. 5.8**).

On further heating from 800°C to 1000°C, the minor amount of magnetite disappeared, probably reduced to metallic iron, which becomes the major mineral phase along with quartz. Another notable observation is that dehydroxylated muscovite starts melting into an amorphous aluminosilicate glass, and that periclase (MgO) is found, most likely as a result of carbonate (ankerite) decomposition (**Fig. 5.9**).

### 5.4.4 Mineral Transformations Relevant to Trace Elements Partitioning in Combustion

From **Table 5.4**, the ratios of Si/Al, Al/K, Al/Ti in all three combustion ash types (BBA, LBA and FA) are comparable within each of the three samples, suggesting the major elements are distributed similarly in all three ash fractions (BBA, LBA and FA). They may therefore be expected to behave in a similar manner during combustion. Three major types of glass phases (Fe-O rich, Fe-Si-Al-O rich, Si-Al-O rich) have been identified under SEM-EDXA. Most bottom-ash-associated trace elements appear to have been partitioned in these three glasses, probably due to the melt and interaction of silicates (clays) and Fe-bearing carbonates (siderite, ankerite) during combustion.

## 5.5 Trace Element Partitioning in High Temperature Ash (400°C)

Trace element behaviour under slow heating has also been investigated, to determine how the combustion temperature and fuel residence time impact on the trace element partitioning behaviour. The selected coal samples (taken from the same seam as the three combustion samples) have been slowly heated to 400°C and then maintained at this temperature until all organic materials have been burnt out, and the resultant HTA ashes were analyzed for trace element contents (**Table 5.6**). The 400°C treatment differs from the stoker combustion regime (that was adopted in the combustion tests of this study) in having lower temperature but longer fuel residence time in the combustion process. It is surprising that some toxic trace elements have been greatly enriched in the HTA ash. For example, the Pb in a ply sample 283-G (ash yield 1%) from southern part of the E seam has been enriched to a very high 1013 ppm relative to coal, whereas the concentrations of

As (26 ppm), Se (13 ppm) and Cr (316 ppm) are much lower (**Table 5.6**). This is an excellent example of adverse consequence of low ash coals. In other samples, the Ba has been enriched ranging from hundreds to 2400 ppm, Ni is up to 1400 ppm, As up to 38 ppm and S up to 19.9% in the respective 400°C HTA (**Table 5.6**). In contrast, Cl is low with <20 ppm, although one sample reached 552 ppm. This observation is quite different from the results of the stoker combustion (which was adopted in the combustion tests of this study) and show how dramatically trace element partitioning behaviour can be influenced by (1) combustion temperature, and (2) fuel residence time stayed in the burner.

## 5.6 Trace Elements Partitioning in Bottom Ash

As previously discussed, the bottom ash is mainly composed of quartz, iron spinel group minerals or glass, and Si-Al-O rich glass. The trace element concentration in quartz of feed coal is very low. The temperature in the combustor (1100°C to 1250°C) is not high enough to melt the quartz, so there is no obvious mineral transformation expected to take place during combustion. Hence it is assumed that no significant amount of any trace elements would be associated with quartz, and trace elements in bottom ash are mainly partitioned in the aluminosilicate and Fe-oxide phases. In order to determine the exact trace element partitioning in bottom ash, three main phases of bottom ash samples (iron oxide, Si-Al-O rich glass, and Si-Al-Fe-O rich glass) have been analysed for trace element by INAA (**Table 5.7**). It was found that, except for Mn, As and Se, the Si-Al-O rich glass has about twice the trace element concentration of the iron oxide phase (**Fig. 5.10**). The iron oxide contains 35 times the Mn (5250 ppm) and 3 times the As (8.52ppm) concentrations of the Si-Al glass. But both (Si-Al-O glass and Fe-oxide) have similar Se concentrations.

Bottom ash is enriched in Sc, Cs, Ba, Rb, in contrast to fly ash which is enriched in As, Sb, Se, Br, Hg, Mn (except Fe-oxides), Zn and W. Rare earth elements and other trace elements seem to partition evenly between bottom and fly ashes (**Tables 5.7** and **5.8**).

## 5.7 Trace Element Partitioning in Fly Ash

### 5.7.1 Float-sink Behaviour of Trace Elements in Fly Ash

Two fly ash samples (P532A-FA and 2A-FA) were also subjected to the float-sink experiment. Major elemental analyses (**Table 5.8**) show that only Fe and Mn (as Fe-bearing oxides or glass) are greatly enriched (7 to 19 times) in sink fractions (with density of 1.64), whereas K and Na have moderate enrichments (1.6 to 2.4 times) in the sink fraction. This is consistent with the mineralogical observations of fly ash samples. The Fe and Mn occur as Fe-bearing spinel group minerals [$(A, B)O_3$ and $AB_2O_4$, where A= $Fe^{2+}$, $Mg^{2+}$, $Ca^{2+}$; B = $Fe^{3+}$]. Fe was also seen in some cases occurring as Fe-S-O glass, possibly as Fe sulfate, $Fe_2(SO_4)_3$. These phases are expected in the sink fraction due to their high specific gravity. K and Na are present in the aluminosilicates or Si-Al glass, and hence could be present in either sink or float fractions depending on the particle size and specific quantity of their host phases.

Overall, all trace elements, except Br, demonstrate moderate enrichment (1 to 3 times) in the sink fractions (density of 1.64) in relation to the float fraction of fly ash. This result suggests that most trace elements in fly ash are predominantly enriched in the inorganic phases, such as Al-Si glass phases and Fe-bearing phases (Fe-oxide glasses). However, some proportion of most trace elements were associated with the float fraction, which consists of predominantly organic-rich incompletely burned charcoal. The organic association of trace elements suggests some other partitioning mechanism, such as absorption and/or adsorption of the trace elements onto the surface of the fly ash particles, may play an important role. The electrostatic properties and large surface area presented by the fly ash make this extremely likely and may explain the float-sink behaviour for trace elements in these fly ash samples.

Mercury is well known as a highly volatile element. In the two fly ash samples (P532A-FA and 2A-FA) analysed by INAA, the fly ash has 424 to 900 ppb of Hg, but no Hg was detected in the respective bottom ashes. It suggests that no appreciable amount of Hg is partitioned in the bottom ash, hence most Hg probably was vaporized. However, only

part of total input Hg (<10%) (see **Table 5.9**) was recovered after combustion. The low Hg recovery was most likely due to the ineffectiveness of the impinger solution used in this study (Clemens, pers. comm., 2001). The Hg probably did vaporise into the flue gas after combustion (because no Hg was detected in bottom ash) but for some reason the impinger solution was not an effective capturing medium. Therefore, it is concluded that Hg probably did partition predominantly into the flue gas (>90%). The small amount (<10%) captured by the fly ash probably did so by dry deposition onto the surface of particles when the flue gas reached the cooler part of the combustion rig. This is consistent with other worker's results (Huang et al., 1996).

Studies of Hg (Huang et al., 1996; Carpi, 1997; Galbreath and Zygarlicke, 2000) have concluded that elemental ($Hg^0$) and divalent ($Hg^{+2}$) are the two major species of this element during coal combustion. Both of these species were found to be highly volatile in this study, and were probably partitioned primarily in the flue gas fraction. While $Hg^{+2}$ is water-soluble and may be removed from the atmosphere by wet and dry deposition close to the combustion sources, the combination of a high vapor pressure and low water-solubility facilitate the long-range transport of $Hg^0$ in the atmosphere. Background mercury in the atmosphere is predominantly $Hg^0$. Carpi (1997) concluded that emissions of Hg from coal combustion sources are approximately 20-50% elemental $Hg^0$ and 50-80% divalent ($Hg^{+2}$), which may be predominantly as $HgCl_2$. The partitioning of mercury in flue gas between elemental Hg and divalent forms may be dependent on the concentration of particulate carbon, HCl and other pollutants in the stack emissions. Because of the high Cl content in Greymouth coals and the enrichment of Cl in the organic matter of the feed coal and because Hg and Cl both vaporize easily during combustion and form $HgCl_2$ in the flue gas, it is very likely that $HgCl_2$ is the dominant form of Hg. $HgCl_2$ formation may have a detrimental environmental impact if concentrations are high.

The depletion of Br in the sink fractions suggests an association with unburned char fragments, which is inherited from an organic association in the feed coal. It is consistent

with the leaching test result that Br is predominantly organically associated in the feed coal (see Chapter 4 for details).

### 5.7.2 SEM-EDXA Observation on Trace Element Partitioning in Combustion Ashes

An attempt was made to locate the hosts of trace elements in fly ash and bottom ash by direct analysis of minerals using SEM-EDXA. However, only a few trace elements were detected because most concentrations were below the detection limit (DL) of SEM-EDXA (usually DL is > 0.1 to 0.5 wt% depending on the individual elements).

#### 5.7.2.1 Fly Ash Trace Element Partitioning

Under SEM-EDXA, Ni was detected in Si-Al glass; Cr and Ni associated with the Fe-rich phase in <2 μm size adsorbed on the unburned char particles of the fly ash; and Zr was occasionally detected in association with quartz in P532A fly ash sample. Submicron-sized Zn was associated with Na-Ca whereas Cl and S were detected in association with Cu, Cu-Fe, or Cu-Fe-Ca oxides, most likely as chlorides and sulphates. A small portion of Cl was also present as salts (NaCl, KCl). Ba was associated with S - probably as discrete grains of $BaSO_4$. Rare earth elements such as La and Ce were associated with phosphate (apatite).

Cu was present as discrete grains (CuO and to lesser extent Cu) or sometimes mixed with Fe oxides; it is common to see Cu as small balls or spheroids, ranging in size from <1 μm to a few microns (up to 8 μm). Cu also coexists as balls or spheroids with Ca-Fe oxides glass (see **Fig. 5.11**), and with CaO glass.

#### 5.7.2.2 Bottom Ash Trace Element Partitioning

Cr was found to be associated with Fe and Mg oxides - most likely as a replacement for Fe. Cl tended to associate with quartz, Si-Al glass or Fe-Mg oxide. All other trace elements were below the detection limit.

## 5.8 Fate and Enrichment of Trace Elements After Combustion

### 5.8.1 Total Input and Output of Trace Elements

The total input of all the trace elements introduced from feed coal before combustion can be determined from the trace element data and the weights of feed coal.

In order to analyse the partitioning behaviour of trace elements during and after combustion, all ash samples were collected and weighed. The proportion of each combustion ash can be calculated in comparison with the total combustion ash. From the trace element data of each combustion product, the contribution of selected trace elements from each ash product [BBA, LBA, FA and flue gas (FG)] can be calculated. The total trace element output can then be calculated by summing up the contributions from all the three combustion ashes. For example, flue gas data show that of the recovered elements, more than 95% of S, up to 64% of Cl, and in some cases, up to 44% B and up to 50% Cd are in the flue gas fractions (**Table 5.9**). Therefore, we can calculate the mass balance of selected trace elements by comparing their total input with their output. If the output of one element is close to the input of that element, it means that element is well balanced and no significant amount of that trace element has been lost into the atmosphere by emission from flue gas. If there is significant loss of a specific trace element in the output compared with that of input, this suggests that this element is highly volatile and has been lost into the atmosphere as part of the flue gas. **Table 5.9** and **Figure 5.12** show the proportion of trace elements in feed coal, BBA, LBA, FA, FG, HTA. **Figure 5.12** displays that most trace elements are partitioned in the bottom ash except for S, Hg and Cl, which are mostly associated with flue gas. Some of the trace elements (e.g., Hg) are recovered with the fly ash probably as a result of either adsorption

or absorption mechanisms because of the large surface area in fly ash compared with bottom ash or as a result of condensation onto the fly ash surface on reaching a cooler part of the combustion rig.

### 5.8.2 Trace Element Partitioning and Enrichment in Different Combustion Ashes

The abundance of selected trace elements in feed coal, BBA, LBA and FA were determined by ICP-MS. The results and their relative enrichment factors (EF) in bottom ash and fly ash relative to the concentration in feed coal are given in **Table 5.10**. In comparison with the trace element concentrations in feed coal, most trace elements are 10 to 300 times enriched in fly ash with the exception of Cl, S, F and B, which show only slight enrichment. Furthermore, even in the combustion ash types, trace elements show very different partitioning patterns in bottom ash and fly ash after combustion. In general, the trace element concentrations are particle-size-dependent and are elevated from coal, big bottom ash, little bottom ash, fly ash. For some elements (Hg, S, Cl, Cd, B), the flue gas fraction has the highest concentration. To determine the trace element partitioning pattern in bottom ash and fly ash, the enrichment factor (EF) is introduced here to quantify the relative enrichment of a specific trace element in the combustion ash (e.g., bottom ash and fly ash) fractions relative to feed coal:

$$EF = C_{ash} / C_{coal} \qquad (1)$$

where $C_{ash}$ and, $C_{coal}$ represents the concentration of trace elements in combustion ash (either fly ash, little bottom ash or big bottom ash) and $C_{coal}$ represents the concentrations in the feed coal. Accordingly, trace elements with different enrichment factors (EF) may be categorised into groups.

### 5.8.3 As, B, Pb and Zn

Group I trace elements are those with moderate enrichments (EF= 2 to 6 in BBA, 3 to 16 in LBA) in bottom ash and significant enrichments in fly ash (EF=11 to 25, **Table 5.10**).

Arsenic and Pb are also among the list of HAPs. There were generally less than 20% of Group I elements (except B) associated with the fly ash fraction, and more than 80% of them were retained in bottom ash, although exact forms were difficult to determine directly due to their low abundance. Most of the trace elements are below the detection limit (DL) of SEM-EDXA, although EDXA did pick up some trace elements, such as Zn. However, it is more likely that these elements were incorporated into the aluminosilicate melt, oxides or glass matrix in the bottom ash. The proportion of these elements associated with fly ash was thought to be absorbed or adsorbed onto the surface of the fly ash particles due to surface area and electrostatic effects.

The behaviour of B and As are of particular interest. B is often found in New Zealand coals at levels significantly above the world mean. As early as in the 1940s, Rafter (1945) noted high B content (up to 1.5% B in Waikato coals) in many New Zealand coals. Arsenic is occasionally found at levels above the mean. All other trace metals are typically present in New Zealand coals at levels close to or below the mean concentrations of worldwide coals. It was found that 44% of the recovered boron was associated with the flue gas fraction of sample 2A (**Table 5.9**). Only 10% and 19% of recovered boron was associated with flue gas for samples P532A and 2B, respectively. This B partitioning behaviour is very different from previously observed in Ca-rich subbituminous Waikato coals (Clemens et al., 2000). In the study by Clemens et al. (2000), they found that >90% B is retained in bottom ash by the formation of borosilicate $Ca_{11}Si_4B_2O_{22}$. However, the lower calcium levels of Greymouth coal ashes has resulted in lower boron retention, although the reason for the significant difference between boron partitioning behaviour of sample 2A compared to the other two samples is unclear. It is interesting to compare the partitioning of these trace metals in this study with that observed previously for highly alkaline sub-bituminous coals from the Waikato. In those studies (Clemens et al., 1999, 2000), it was found that approximately 90% of the boron recovered and 60% of the arsenic were associated with bottom ash – not the sort of partitioning associated with what are traditionally regarded as volatile elements. This unusual partitioning behaviour is ascribed to the highly alkaline nature of the coals and the combustion regime used to burn them. The coal ashes are rich in calcium (up to 55%

CaO in ash) and calcium boro-silicates were formed during the heating of the low temperature ashes. High arsenic retention was attributed to formation of calcium arsenates.

However, for the combustion tests of the Greymouth coals, the coal ashes are comparatively low in calcium, no calcium boro-silicates are observed among the heated low temperature ashes, and the boron and arsenic retention levels remain fairly high. This suggests that the stoker combustion regime itself – a static bed, long retention times, large coal particles and moderate temperatures – are the major reasons for the high retention of trace metals traditionally regarded as being highly volatile. Another possibility, of course, is that the elements are originally present in the coal in forms that survive the temperatures within the firebox during combustion. The leaching tests performed on these three samples show no difference in leaching behaviour. No more than 5% of B is removed in $CH_3COONH_4$, HCl, HF sequential leaching steps, and only 10-15% of B leached by $HNO_3$, suggesting a majority of B is associated with organic matter in these three feed coal samples. However, 10% to 44% of B recovered was partitioned in flue gas.

In the case of Strongman coal sample 2A, the concentration of boron recovered from the flue gas is noticeably higher than that from the other two coals used in this study and significantly higher than that seen in any of the Waikato coal studies. There is up to 44% of recovered B partitioned in flue gas in sample 2A, whereas only 10% and 20% of recovered B in their counterpart in sample P532A and 2B, respectively. However, the total B recovery for all these three samples is in the range of 20% to 40%. There are no obvious reasons for this difference in behaviour. The calcium concentration of this coal is much lower than that of the Waikato coals but is similar to that in samples P532A and 2B. The only major difference in the ash analysis data is the high silicon and low iron concentration found in this sample but it is difficult to understand how that translates into a decrease in boron retention. It is, however, a good example of how variable the partitioning behaviour of trace metals can be – even between samples taken from the top

(2A) and bottom (2B) of the same seam. With the conflicting data presented here and in other studies, is clear that B partitioning is still not fully understood.

In a study of leaching of boron from Illinois coal ash, Cox et al. (1978) found that about 50% of the B content (1900 ppm) in fly ash was leachable into water, and the leaching rate was even greater in acid solution but was independent of pH over the range of 6-8; in contrast, he found B content (960 ppm) in bottom ash was essentially insoluble. Cox et al. (1978) further reported that a 1200°C treatment of ash for 30 minutes decreased the leachable B in fly ash to 6% of the total B.

In a study of the leachability of B from combustion ash in Huntly Power Station of New Zealand, Wilkinson (1985) noted that the drainage water resulted from weathering of combustion ash contain high B content (0.2 to 3 $g/m^3$ at pH of 6.1 to 6.5, even the water collected from the nearby boreholes contains on average 0.23 to 1.47 $g/m^3$ of B at pH of 6.1 to 6.5.

The total recovered As in the three combustion experiments conducted as part of this study ranges from 22 to 37%. As often behaves as a volatile element, but in the present case, 84% to 90% of recovered As fails to leave the firebox, with only 10-16% of the As partitioned in fly ash. This As partitioning relates to its association with clay minerals in feed coal (E seam) which is supported by coal leaching test results (see Chapter 4). The leaching tests demonstrated that up to 45% of As was removed by HF and less than 5% was leached by $HNO_3$, suggesting a pronounced silicate (clays) association. It is highly likely As is present as sub-micrometer inclusions in clays, because up to 45% of As is not released until the dissolution of clays; Reimann and Caritat (1998) reported that " In water bodies, As is removed relatively fast from the water and loosely bound into the sediment, or adsorbed to Fe-hydroxides and clay". After the clay melts during combustion, a large proportion of the As remains trapped within the resulting iron oxide glass.

In a study of coal combustion products of the Appalachian coals (0.65-1.98% S, 10-11% ash) and high-sulphur Illinois coals (4.57% S, 9% ash), Hower et al. (1993) found that elements commonly associated with sulphides, notably, As, Mo, Ni, Pb, V and Zn were higher in ash from high sulphur coals. In addition, leachate from the standard toxic chemicals leaching procedures (TCLP) of the fly ash derived from high S coals were also higher in As and Pb than the low-S ash leachate.

Zn and Pb have surprisingly similar behaviour in combustion. Both Zn and Pb increase their concentration dramatically from big bottom ash, little bottom ash to fly ash. In terms of proportion of total elements, there is 85 to 95% of Zn and 83 to 91% of Pb portioned in bottom ash with the majority partitioned in little bottom ash. There is 5 to 15% of Zn and 9 to 17% of Pb partitioned in fly ash. Further study of these two elements in bottom ash and fly ash reveals that Zn is chiefly partitioned in silicates. For example in the bottom ash of sample 2A, three major components of bottom ash have been analyzed for trace elements by INAA; Si-Al-O silicate has the highest Zn (142 ppm), the Fe-oxide the lowest Zn (53 ppm), and silicate with Fe has Zn (125 ppm) with proportions between the former two components. This suggests that Zn is mainly enriched in the Si-Al-O phase rather than Fe-bearing oxides in the bottom ash. The feed coal leaching experiment results illustrate that 30-70% and 20-50% of Zn were removed by HCl and HF, respectively; moreover, no Zn was removed by $HNO_3$. All of the above results consistently support the conclusion that Zn is associated with silicates (clays) in feed coal, and partitions in silicates in bottom ash after combustion. This finding is in contrast to some previous studies, which traditionally regarded Zn as sulphide association in coal (Finkelman, 1981; Swaine, 1990).

Pb behaves surprisingly similarly to Zn (see **Tables 5.9 and 5.10**). Moreover, As, Pb, Zn, Cd and Hg have a strong correlation with S ($r > 0.8$) in combustion ash and there are also good inter-elemental correlations between these elements. But in the coal, Pb does not correlate with S (Li et al, 1999, 2001b), so it can be inferred that it is not occurring predominantly as a sulphide (PbS) in coal. The good correlation of Pb and other elements

in this group with S in combustion ash suggests during combustion, these elements are volatilized along with S, and react with each other to form sulphates.

### 5.8.4 Hg, Se, Cd and Cu

In contrast to the Group I elements, the Group II trace elements are characterized by not only a significant enrichment (EF =10 to 40) in fly ash and with moderate enrichment (EF <10) in bottom ash, but also with a significant proportion partitioned in fly ash. This group of elements is known to be highly volatile. As expected, they vaporized and escaped from the firebox during combustion, and chiefly partitioned in flue gas and/or fly ash either by absorption, adsorption or condensation after reaching cooler parts of the combustion rig. However, the total recovery for this group in all three combustion runs is not high (Hg 5% to 10%, Cd 7 to 50%, and Se 10 to 42%; **Table 5.9**). But within the total recovery of this group of trace elements, around 80-100% Hg, up to 40% Cd, and 40-70% Se have partitioned into the fly ash (see **Fig. 5.12**). The balance of those trace elements have partitioned in the bottom ash. However, it was also observed that up to 50% of Cd was partitioned in flue gas in one (2B) out of three samples. Nevertheless, the recovered Hg is coincidently and predominantly partitioned in fly ash with concentrations of 0.53 ppm, 1.1 ppm and 0.63 ppm in fly ash samples P532A-FA, 2A-FA and 2B-FA, respectively. In contrast, Hg in bottom ash ranges from undetected to <0.015 ppm. It is widely accepted that the majority of unrecovered Hg is partitioned in flue gas because it is known to have a high volatility. Further study of fly ash partitioning, by float-sink tests with heavy liquid of specific gravity (Sp.G.) of 1.64, shows that the Hg has twice the concentration in sink fraction in one sample, whereas it is only slightly enriched in the float fraction of the other sample. This ambiguity indicates that the absorption, adsorption and/or condensation mechanisms also played an important role on the Hg partitioning in the fly ash. If this is the case, then this type of Hg is readily available for mobilisation.

The partitioning behavior of Se differs between sample 2B taken from the bottom of the seam and sample 2A taken from the top. When the sample (2B) from the bottom of the seam was combusted, the majority (68%) of the recovered selenium escaped the firebox

and was recovered in the fly ash. When the top sample (2A) was combusted, only 5% of recovered Se partitioned in fly ash but the majority (95%) of the recovered selenium was associated with bottom ash. It suggests that the selenium is bound up in a non-reactive form in the coal from the top (2A) of the seam but much more loosely associated in the sample from the bottom (2B) of the seam. The sequential leaching tests described in Chapter 4 show no significant difference in selenium behaviour between samples 2A and 2B. In the sequential leaching tests on coal samples, both samples 2A and 2B have very low percentage (<5%) of Se removed by any of the four leachant acids, suggesting a predominantly organic association. Alternatively it may be that the high Si low Fe ash formed during combustion of the top sample (2A) undergoes a fundamentally different chemistry from that of the comparatively low Si, high Fe ash formed during combustion of the sample from the bottom (2B) of the seam. This could impact on the selenium partitioning behaviour although there is nothing in the series of ashes generated by heating the respective low temperature ashes to support this explanation. The only significant difference between the two series is that under reducing conditions, metallic iron is formed in much greater quantities (and is detectible at lower temperatures) from the high iron sample than from its low iron counterpart. This is not an unexpected result and offers no obvious explanation for the difference in selenium partitioning behaviour.

Copper (Cu) was apparently and unfortunately contaminated in the combustion run for sample P532A. The combustion run for P532A followed a combustion test for a Cu-treated timber combustion run, and although all possible efforts were made to clean the combustion rig beforehand, it is obvious some contamination remained. However, the mass balance of Cu in combustion of 2B is almost perfect with total recovery of 106%. Despite the influence of Cu contamination from Cu-treated timber, a general trend of Cu partitioning chiefly (50 to 80%) in fly ash is evident.

### 5.8.5 S and Cl

Group III includes highly volatile elements S and Cl. S is significantly enriched (EF = 10 to 15) in fly ash but depleted in bottom ash. Chlorine is only moderately (EF = 1 to 2)

enriched in fly ash but uniformly depleted in all bottom ash samples. Both S and Cl are regarded as highly volatile but with the majority of recovered elements partitioned in flue gas fraction. There is 91% to 97% of the total recovered S and up to 64% of Cl recovered from the flue gas fractions (**Table 5.9**).

Up to 70% S retention in bottom ash may sometimes be observed for high calcium coals (Clemens, pers. comm., 2001). For these low calcium Greymouth coals it is expected to find a significantly lower level of retention.

The high proportion of S (as SOx) escaping the firebox is not unexpected. In some of the highly alkaline sub-bituminous industrial coals from the Waikato, a significant amount (in excess of 20%) of the sulphur is sometimes retained in bottom ash. This is largely due to the high calcium concentrations in the ash of these North Island coals. This can reach as high as 55% CaO in ash (Clemens, 2001, pers. comm.). The chemical reaction responsible for the S retention is

$$CaO + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 \qquad (2)$$

For these bituminous West Coast coals with their much lower concentrations of calcium, the tendency toward sulphur retention is much lower.

In the combustion tests, 64% of the total recovered Cl partitioned in the flue gas was only observed from sample 2B. In another experiment using an electric furnace, it was found that <1% Cl was retained in the resultant ash after heating the three coal samples to 400°C. These tests confirm that most Cl has left the combustion chamber during the early combustion stage. It suggests that the Cl is predominantly loosely-bound with organic matter, and/or occurs as salts (NaCl, KCl) as observed under SEM-EDXA. If this is the case, Cl could easily become volatile after heating to 400°C or higher.

### 5.8.6 Co, Cr and Ni

Group IV includes Co, Cr and Ni. In the float-sink tests of feed coal, Ni and Co show no clear distribution pattern, although they are relatively enriched in float fractions. In the leaching tests of feed coal, up to 70% of Cr was removed by HF suggesting an obvious silicate association. However, only 5 to 10% of Co and 5 to 15% of Ni were removed by HF and the total leached percentages of these two elements are very low.

In bottom ash, Cr and Co have approximately double the concentrations in silicates compared with Fe oxides. In fly ash, Cr and Co are significantly enriched in sink fractions (Sp.G. 1.64).

In terms of partitioning proportion among different combustion ashes, Co, Cr and Ni are all predominantly (>90%) partitioned in bottom ash, especially in little bottom ash (>60%). This combustion behaviour is very much the same for Zn and Pb.

### 5.8.7 Ba, V, Zr, Rb, Sr, F , REE, Th and Y

Group 5 elements include Ba, V, Zr, Rb, Sr, Th, F, La, Ce, Ga and Y . This group of trace elements is commonly associated with silicates in igneous and sedimentary rocks. In the present study, they are associated with silicates (mainly clays and quartz) in the coal and enriched in the sink fraction (**Fig. 5.2**). Unlike the first four groups of elements, the elements assigned to the fifth group tend to be depleted in fly ash and enriched in bottom ash, with a much higher EF in bottom ash than fly ash. Under SEM-EDXA examination of feed coal samples, Zr was detected as inclusions in quartz and clay, the rare earth elements occurred as phosphate. Th and Ba were present in clays. The elements assigned to the fifth group are not only directly or indirectly (e.g. as inclusions) related to aluminosilicate and quartz but also they are well correlated with each other, especially V, Cr, Th, Nb, Ga, Y, Zr, and Rb. Barium, Zr, Sr are also well correlated with La and Ce. This possibly relates to phosphates associations in the feed coal.

The other trace elements show no clear enrichment or depletion in bottom ash or fly ash, and uniformly partitioned between both. They are most likely associated with fine quartz or clay minerals. During combustion, they can partition into either bottom ash or fly ash dependent on their mineral grain size in the feed coal.

The elements assigned to the fifth group were predominantly (>90%) partitioned into bottom ash after combustion. These elements are most likely partitioned in silicates and aluminosilicate glass matrix. These elements are associated with mineral matter in feed coal. After combustion, these elements are presumably strongly bonded or encapsulated within these aluminosilicate or glass matrices. If this is so, it is not expected that these elements are readily leachable from the refractory aluminosilicate and glass matrix, unless under highly acidic conditions. Therefore it may be predicted that the elements assigned to the fifth group will remain within the ashes and that from this viewpoint these ashes are more environmentally safe for disposal and/or utilisation than all previous four groups.

An attempt was made to look at how temperature affects the trace elements partitioning when combusted under different temperatures. A simple comparison between the combustion ashes (under 1100 to 1250 °C )(BBA, LBA, FA) and their respective HTA obtained from 750°C ashing process in an electric furnace was made. When comparing the trace element concentrations in combustion ashes (BBA, LBA, FA) with their respective 750°C HTA (**Table 5.11**), most elements, apart from Cl and Se, have closely comparable concentration levels in both combustion and HTA ashes. This suggests that most of the trace elements behave in a similar manner at or above 750°C.

Fluorine, Y and REE are predominantly (>95%) partitioned in bottom ash, and this is attributed to their association with phosphates in the feed coal (see Chapter 4). Phosphates such as apatite and monazite have been identified in the coal by XRD. Y, Th and REE have been detected in SEM-EDXA. F was not found because its concentration (hundreds of ppm) is well below the detection limit (>1%).

Fluorine and many F compounds are highly toxic (Reimann and Caritat, 1998). Because F is very volatile, it is commonly found that most of F is recovered from fly ash or flue gas under pulverized coal combustion (PCC) and fluidized bed combustion (FBC) systems. However, in the present case under stoker fired combustion conditions more than 90% of F is retained in bottom ash. This abnormal F partitioning phenomenon may be attributed to the occurrence of F as phosphate in the feed coal, this is also supported by the fact that up to 91% of F is enriched in sink fractions in all three feed coal samples. In another experiment undertaken in this study, it was found that the majority of F was also retained in ash after ashing the coal to 400°C. When the coal was burned, phosphates remain stable and along with the fluorine are retained in bottom ash. Even though some phosphate broke down and reacted with Al-Si melt glass, F reacted with Ca, formed $CaF_2$ and stayed in the bottom ash.

Rare earth elements (REE) also occurred in phosphate minerals (see Chapter 4). Their predominant partitioning with bottom ash is not surprising because most phosphates would be expected to be retained in bottom ash. A small proportion of sub-micrometer phosphates may have carried over as fly ash due to the upward thermal dynamic flow in the combustion system.

## 5.9 Discussion on the Environmental Significance of Trace Elements in Combustion Ashes

The hazardous effects of some trace elements (e.g. As, Hg, Pb, F, etc.) to the environment have been long recognised. Most coal combustion by-products are disposed of close to coal-fired power stations. Although coal combustion products were declared as non-hazardous materials by the US Environment Protection Agency (EPA), a high concentration of some trace elements, especially HAPs in any combustion ashes, could potentially cause undesirable environmental effects unless they are present in unleachable forms, for example, in mineral structures with strong molecular bonding. For example, the U.S. Environmental Protection Agency (EPA) (1998a, 1998b, 2000) cited in a report

that Hg emissions from electric utilities as the largest remaining anthropogenic source of Hg released to the air. The US EPA (1998a, 1998b) reports that "Concentrations of Hg in the air are usually low and of little direct concern. Once Hg enters into waters, either directly or through air deposition, it can bioaccumulate in fish and animal tissue in its most toxic form, methylmercury. Bioaccumulation means that the concentration of Hg in predators at the top of food web (for example, predatory fish or fish-eating birds and mammals) can be thousands or even millions of times greater than the concentrations of Hg in the water...". Human exposure to Hg occurs primarily through eating Hg-contaminated fish and has been associated with serious neurological and developmental effects in humans. Therefore, understanding how the trace elements are partitioned in combustion ash is more important than knowing what their concentrations are, for it allows us to assess what the potential environmental impact might be for the disposal or utilisation of combustion ash.

Fly ash generally contains at least two (or more) folds concentration of most trace elements (such as As, Be, Cr, Hg, Pb, etc.) than bottom ash. Nevertheless, the trace elements partitioned in bottom ash usually have been associated with glassy and refractory silicates or Al-silicates, and they are difficult to mobilise unless under some extreme conditions (e.g. long exposure to very acidic conditions). In contrast, trace elements associated with fly ash are in much more loosely-bonded forms, chiefly absorbed/adsorbed on particles as in this study, hence they have a higher tendency toward mobilisation, even under typical natural conditions. The mobilisation of those trace elements, especially HAPs, is the major concern for the environment and the human health. Therefore, most work on the environmental impact of trace elements associated with coal combustion has focused on fly ash. Wright et al. (1998) studied root growth and trace element uptake in acid soils treated with coal combustion by-products, and concluded that ryegrass concentrations of Cu, Zn, Ni, Pb, Cd and Cr were similar in treated and untreated soil, whereas B, Se, As and Mo were increased in ryegrass growth in treated soil. However, Se from fly ash was the only potential food chain risk from a single application of these materials. Codling and Wright (1998) also concluded that fly ash and scrubber sludge increased Se, As and Mo concentrations in ryegrass but only Se

from fly ash would present a potential food chain risk. When Fleming, et al. (1996) studied the leachability of metals from coal combustion fly ash, they concluded from their column leaching experiment results that a decrease in the pH of the leachant increases the extraction of metal ions from solid particles of fly ash. The significant increase in the extraction of Cd, Cr, Zn, Pb and Hg ions from the ash was attributed to the chemical instability of the mineral phases that contain these metals under acidic conditions. Dudka and Miller (1999) studied the risk assessment of the environmental hazard related to As and Pb in contaminated soil, and reported that As and Pb concentrations in soil can reach 40 μg/g and 300 μg/g without a hazard to exposed organisms.

In the present case, the combustion ashes (bottom and fly ashes) contain all the above-mentioned trace elements, including those on the list of HAPs in the US 1990 Clean Air Act Amendments. Because of their well-known toxicity, it is prudent to utilise or dispose of combustion ashes with care; otherwise they may cause undesirable environmental impacts. Fortunately, because of the relatively low trace element concentrations in fly ash compared to combustion fly ashes around the world (**Table 5.12**), there should not be a great concern arising from the combustion of the Greymouth coals. However, the low ash yield in the Greymouth coals also has a negative effect. Because most of trace elements including environmentally sensitive elements are enriched in ash, the low ash coal can greatly enrich some of these toxic trace elements in the combustion ashes. For example in combustion test of a relatively low ash sample (2B, with 3.3% ash), the B concentration in the little bottom ash and fly ash have been enriched to 1100 ppm and 1000 ppm, respectively. The B in the fly ash of the other two combustion tests 2A and P532A also have enriched to 560 ppm and 610 ppm respectively. This high B content in combustion ash may cause toxicity to the environment. Cox et al (1978) reported that about 50% of the B content (1900 ppm) in fly ash of the Southern Illinois coals was leachable into water and the leaching rate was even greater into acid solution, although the B content (960 ppm) in the bottom ash was essentially insoluble. In a study of radiata pine culture seedlings, De Lanuza (1969) found that B toxicity symptoms became progressively severe for the leaf with increasing B levels from 100 to 3700 ppm, and irreversible

necrosis occurs at B levels greater than 1000 ppm. Bradford (1963) and Jones (1972) have stated that although B tolerance by plants varies with species and stage of growth, B levels greater than 200 ppm are usually associated with toxicity symptoms. Smidt and Whitton (1975), in a study of damage to gradually dying radiata pine (*Pinus radiata*) in a vicinity of a boiler-house near Waipukurau, Central Hawkes Bay, concluded that B toxicity to the trees was attributed to: (1) dumping of furnace ash and clinker with high B content (1900 ppm) in the gully containing the pine plantation, thus ground water percolation and washing downslope made high B available for absorption by the trees; (2) fly ash falling from the furnace chimney to the trees. Smidt and Whitton (1975) suggested that a level of approximately 200 ppm B in the needles is necessary to produce B toxicity symptoms in mature radiata pine. In the present study, the high B (>1000 ppm) in the fly ash may cause toxicity to some plants such as radiata pine. Previous investigations (Holliday et al., 1958; Cope 1962; Wilkinson, 1985) of waste ash from electric power station burners have suggested that B is the most important toxin present. Cope (1962) and Hodgson and Holliday (1966) reported that B toxicity in dumped ash persisted for many years. Aitken and McCallum (1988) reported B toxicity in soil solution.

Although a comprehensive environmental impact assessment on the Greymouth coal combustion is beyond the scope of this study, some general comments and suggestions can be made based on the combustion results of this study.

(1) Compared to the trace element contents in fly ash around the world, most trace elements in Greymouth coal fly ash are below the overseas mean concentrations (**Table 5.12**). The exceptions are B, S and Cl. The highest concentration of B, S, Cl was found to be 1100 ppm, 4.41% and 2000 ppm, respectively. The high content of B, S, Cl in the combustion ash may cause undesirable environmental concerns in the vicinity area of the coal combustion site. Some of the toxic trace elements may also be mobilised and released to the environment. For example, Karuppiah and Gupta (1997) studied leaching of metals from land disposal of coal combustion ash and concluded that toxicity and metal (As, Cd, Cr, Cu, Fe, Pb, Ni, Ag, and Zn) concentrations of leachate were highest

when ash was leached with HCl at pH 4. In another study of mobility of heavy metals from six different coal-fire power plant fly ashes, Fernandez-Turiel et al. (1994) reported that Cd, Co, Cu and Zn show the highest extractable fraction (10.8%-18.9% on average, up to 36.4% Zn), with Cd (4.7% to 15.7% of total Cd) and Sb (0.24% to 10%) being the most easily water-extractable elements. Ni and Pb have relatively low potential mobility with average 5.5% and 5.3% of total content, respectively.

If the combustion ashes of Greymouth coals, especially fly ash, are disposed of and exposed to long periods of acidic conditions, it is prudent to monitor the mobility of those toxic trace elements, especially HAPs. Black and Craw (2001) recorded 0.7 ppm As (winter season) and 1 ppm Zn in water discharging from waste piles created from an opencast coal mine in southeast Otago, New Zealand, although As and Pb at these levels were not significantly hazardous.

(2) Although >90% of Cr partitions in bottom ash associated with refractory Al-silicates, and is hence unlikely to mobilise, Cr was found locally occurring in a very toxic form ($Cr^{6+}$) as crocoite ($PbCrO_4$) (Li et al 2001b) at some intervals in Greymouth coals. Lead was also found in elevated concentrations locally at those coal seam intervals containing crocoite. The run off and drainage waters in the West Coast coal mining areas are often acidic with pH < 4, and this is a favourable condition for the mobility of some toxic trace metals including $Cr^{6+}$. It would be a good idea to monitor the mobilisation of those toxic trace elements, especially $Cr^{6+}$, in the underground waters in the vicinity of coal mining area.

(3) In the present case, most Hg (>90%) was partitioned in flue gas. However, all recovered Hg (<10%) partitioned in fly ash by absorption, adsorption and/or condensation mechanisms. This loosely-bonded partitioning type of Hg, can lead to a high risk of Hg mobility under acidic conditions. Mercury chlorination (i.e., formation of $HgCl_2$) is generally assumed to be the dominant mercury-transformation mechanism in coal combustion flue gas. The high concentration of Cl in Greymouth coals makes $HgCl_2$ very likely the dominant Hg partitioning in flue gas and/or fly ash. Hg is long recognized

as being a very toxic trace element. Hg can evaporate when released to water or soil. Microbes can convert inorganic Hg to organic forms, which then can be bioaccumulated in aquatic life (e.g. fish accumulate methyl-Hg). Uptake of methyl-Hg via eating contaminated aquatic organisms can cause minamata disease (Reimann and Caritat, 1998). The US EPA suggests that Hg in drinking water exceeding action levels (0.0005 to 0.002 mg/l) can lead to kidney dysfunction and damage in the short term. Given the low concentration of Hg in feed coal and combustion ash, however, it would be very surprising for any major undesirable impact arising from the combustion of the Greymouth coal.

In summary, because of the generally low concentration of most trace elements in comparison with other coal combustion ashes from around the world, it is not expected that significantly undesirable environmental impacts will arise provided necessary caution has been taken to minimise the potential release of trace elements in the disposal process. However, some HAPs ($Cr^{6+}$, Pb, and Hg, etc.) with high potential for mobilisation do exist in Greymouth coal and combustion ashes, although in relatively low concentrations. If those HAPs are leached into waters under acidic conditions with pH <4, they may cause some kind of contamination and it would be prudent to monitor those HAPs in the waters (surface and subsurface waters, but especially drinking and irrigation waters) in the vicinity of the combustion ash disposal site. Nevertheless, these issues should be treated on a case by case basis.

## 5.10 Conclusions

The behaviour of some environmentally sensitive trace elements in float-sink tests and their partitioning in different combustion ashes have been illustrated quantitatively based on the respective proportion in different ash types generated from the laboratory-scale combustion runs. The mineralogical transformation during coal combustion has been investigated in relation to the trace element partitioning in bottom ash and fly ash. The partitioning mechanisms of those trace elements during stoker fired combustion has been determined and discussed. In summary, the following conclusions can be derived:

1. Although the low ash Greymouth coals have the advantage of generating less solid combustion ash, one of the accompanying consequences is that they can enrich the trace element content in the ash to a surprisingly great magnitude upon combustion. For example, B, S and Cl have been enriched to undesirable levels of 1100 ppm, 4.4% and 2000 ppm, respectively.

2. Trace elements have been categorised into five different groups in terms of their differential partitioning patterns in flue gas, fly ash and bottom ash.

Group I (As, B, Pb, Zn) significantly, and to a lesser extent Group II (Hg, Se, Cd, Cu) elements, are significantly enriched in the fly ash fraction. Most of these elements are on the list of HAPs and should be treated with caution if disposal and/or utilisation are considered. However, the concentration for most trace elements in this case are in the low concentration range compared with other overseas combustion ashes. B and, occasionally, As are exceptions. They are often regarded as very volatile but they were found to be mainly retained in the bottom ash in this case, due to a silicate association in the feed coal. They are unlikely to be leached in large proportions particularly if the pH does not become too acidic (pH <4) in the combustion ash disposal sites.

Group III ( >90% of the S and up to 64% of the Cl) and some toxic elements from Group I and II [ >90% Hg, and to a lesser extent B (up to 44%), Cd (up to 50%), etc.] tend to be dominantly partitioned in the flue gas fraction, whereas most other trace elements mainly partition into the bottom ash fractions. More than 90% of Hg appears to be partitioned in flue gas, but part of Hg (<10%) is probably absorbed and/or adsorbed onto the surface of fly ash particles with the concentration ranging from 0.4 to 0.9 ppm; this part of the Hg is likely to be mobile under acidic conditions. Cl is present in high concentrations in Greymouth coals compared with the mean of coals worldwide.

In contrast, elements assigned to the fourth group (Co, Cr, Ni) and the fifth group (Ba, V, Zr, Rb, Sr, F, REE) are chiefly retained in the bottom ash and probably encapsulated or

cemented in the aluminosilicate or glass matrix. They are not easily leachable unless under extreme conditions. Fluorine was also partitioned in bottom ash probably due to its phosphate association in feed coal.

3. The Pb abundance is relatively low in feed coal, but two other factors must be taken into account for its environmental impacts.

The general low ash content of the feed coal means that trace elements may be greatly enriched in the combustion ash. For example, Pb, As, and Se concentration reach a very high 1013 ppm, 26 ppm, and 13 ppm, respectively, in 400°C HTA ash of sample 283-G. Likewise some other trace elements have also been greatly enriched including Ba (up to 2400 ppm), As (up to 38 ppm), Se (up to 30 ppm), Ni (up to 1413 ppm) and S (up to 20%). The very different observation obtained under stoker combustion and slow heating conditions in this study suggests that the trace elements behaviour is largely determined by combustion temperature and fuel residence time during coal combustion;

The unusual mode of occurrence of Pb in the mineral crocoite, may play a different role and change its behaviour upon combustion.

# Chapter 6

# Chapter 6 Main Conclusions

## 6.1 Mineralogy and Low Ash Greymouth Coals

Both the Main and E seam coals in the Greymouth coalfield are characterised by extremely low ash contents (in some case <0.6%) and great thickness (up to >35 m). The mineralogy of both seams is relative simple. Kaolinite, illite, quartz and pyrite are the major minerals in the Main seam, whereas kaolinite, illite, quartz, siderite and ankerite are the dominant minerals in the E seam. Minor to trace amounts of phosphate, sulphate, crocoite and other minerals are also present in both seams.

Clay minerals were found to occur in at least three distinctive forms (syngenetic, epigenetic and clay conglomerates), which are probably related to their formation at different stages or under different conditions. Whereas secondary cleat or fracture-filling, epigenetic clays have much lower trace element contents, finely-crystalline syngenetic clays contain most of the trace elements in the coal. Pyrite is also present in three different forms (syngenetic, epigenetic, and cluster pyrite); these were apparently formed at different stages as well.

Taking into account previous studies on sedimentology, paleotopography, basin depositional setting and development, the results from this study favour two previously proposed detrital sources (NW and east of the basin) which supplied inorganic constituents to the Greymouth coal basin. The surprisingly similar REE patterns of coal samples and basement rocks are strong support for the above conclusions concerning the sources of detritus.

One of the most interesting features of the Greymouth coals is their extremely low ash content, even lower than some modern peat deposits. The unusual low ash contents (mostly 0.6 to 3%) occurring in such a thick (up to 35m) and reasonably extensive coal seams are hard to explain by the usual models in the literature. Based on all observations of this study, two hypotheses have been proposed to explain the low ash nature of the

Greymouth coals. Several lines of physical and chemical evidence (e.g., etched features on clays and quartz, and mobilization of void–filling liptinitic materials) seem to favour the interpretation that peat and post-burial leaching mechanisms may have been operating and helped to move some inorganic constituents out of the coal seam, hence lowering the ash content of the Greymouth coals.

## 6.2 Trace Elements in the Greymouth Coals

This is the first comprehensive case study dedicated to the investigation of the trace elements in both the Cretaceous Main and E seams of the Rewanui Coal Measures of the Paparoa Group. This study first reported the concentrations and spatial distributions of the trace elements in those coal seams, and a particular focus has been on determining their modes of occurrence (e.g., physical and chemical hosts) in the coal. Trace elements behaviour upon combustion has been investigated through three laboratory combustion tests. Finally, the potential environmental impacts of trace elements during mining and combustion have been assessed based on their modes of occurrence in the feed coal.

The concentrations of all trace elements of interest are relatively low compared with other overseas coals of similar rank and age, although a few environmentally-sensitive elements (As, Pb, Cl) can be locally enriched. For example, As reaches 21 ppm and Pb reaches 27 ppm in some horizons of the Main seam. In the E seam Pb can attain concentration of 121 ppm. Although the horizons with high As and Pb contents are not commonly found over a wide area, they should be treated with caution, especially for export coal products. To maximize its value, Greymouth coals have been marketed as a unique premium coal to international markets and have attracted significant interest. Some coal users do have special requirements, such as maximum acceptable concentrations for some trace elements. Unrepresentative sampling must be avoided so as not to misrepresent trace elements.

Because of their low concentrations, it is impossible to determine the mode of occurrence of trace elements by directly analysing the hosts. Thus, a group of direct (SEM-EDXA

and electron microprobe determination of trace element-bearing minerals, INAA analysis of trace elements in minerals) and indirect but complimentary (float-sink, sequential leaching, inter-elemental correlation) techniques and approaches have been used to determine the modes of occurrence of trace elements in the Greymouth coals.

In summary, the modes of occurrence of trace elements in the Greymouth coals are:

(1) Most trace elements including some HAPs (As, Be, Cr, Hg, Sb and U), traditional silicate-associated elements (Rb, Sr, Sc, V, Li, W, Zr) and other elements (Ba, Cs, Hf, Mo, Sn, Tl and Zn) have been dominantly associated with minerals (mainly clays) in the coal;

(2) In contrast, some trace elements (B, Br, Cd, Cl, Co, Ni and Se) were found to be organically bound or as sub-micron-sized minerals intimately admixed in the organic matrix.

(3) REE, Th and Y demonstrate strong association with phosphate with a predominant percentage being $HNO_3$ soluble.

Moreover, some new and/or very interesting findings have been made in the course of this study:

(4) Crocoite ($PbCrO_4$), a rare mineral usually only occurring in the oxidizing zone of Pb deposits, was found in the coal as a major host for Pb and $Cr^{6+}$(which is the most toxic form in any Cr compounds), although most Cr (as $Cr^{3+}$) is present in clay (illite). This is the first reported occurrence of crocoite in coal. Crocoite accounts for the intervals with locally high Pb concentrations found in both the Main and E seams. The run-off and drainage waters in the West Coast coal mining areas are often acidic with $pH < 4$, which is a favourable condition for the mobilization of some toxic trace elements, including Pb and Cr.

(5) In contrast to the "maceral association" of Cr in US bituminous coals (Huggins et al., 2000), Cr was found to occur mainly in illite (in addition to the unusual occurrence of crocoite in the Greymouth coals).

(6) Some elements widely believed to be associated with sulphides, namely As, Hg, Sb and Zn, were found to be mainly associated with clays.

(7) In addition to the uncertain "organic association" of Co and Ni reported in other coals, a significant proportion of Co and Ni were found to be mainly associated with sub-micron-sized clays which are intimately dispersed throughout the organic matrix.

## 6.3 Trace Elements in the Combustion Products

Using three combustion tests, trace element behaviour has been described in terms of their fate and partitioning to different combustion product fractions (e.g., bottom ash, fly ash or flue gas).

In summary, the partitioning of trace elements in combustion ashes is as follows:

(1) Most trace elements including some HAPs (As, Co, Cr, Ni, Pb, and in some case Cd and Se) and other elements (Ba, F, La, Ce, Ga, Nb, Rb, Sr, Th, V, Y, Zn and Zr) are found to be predominantly partitioned in bottom ash.

(2) For those trace elements predominantly partitioned in bottom ash, trace element contents in the three major phases (Fe-oxides, Si-Al-O silicate glass, and Fe-bearing silicate) of the bottom ash have been investigated. Whereas As and Mn dominantly partitioned to Fe-oxides, most trace elements listed in (1) were partitioned between the other two phases, especially into the Si-Al-O rich glass. These trace elements are generally encapsulated or cemented in the aluminosilicate glass and should normally be unavailable for mobilisation unless under extreme conditions.

(3) In contrast, some toxic elements [>90% of S, >90% of Hg, and to a lesser extent, B (10 to 44%), Cd (up to 50%) and Cl (up to 60%)] were found to be chiefly partitioned in the flue gas fraction. However, a proportion of Hg (<10%) is probably absorbed onto the surface of fly ash particles (0.4 to 0.9 ppm), and this fraction of Hg may be freely released into the soil or water.

(4) Although the low ash Greymouth coals have the advantage of generating small volumes of solid combustion ashes, one of the consequences is that combustion can enrich the trace elements in the ashes very significantly. For example, B, S, and Cl were enriched to 1100 ppm, 4.4% and 2000 ppm, respectively.

## 6.4 Environmental Impacts Associated with the Greymouth Coals and Their Combustion Products

Due to the relatively low contents of trace elements in the Greymouth coals, no major hazardous environmental impacts are expected in the coal mining areas. However, the unusual occurrence and potential toxicity of crocoite ($PbCrO_4$) should be treated with a great deal of caution. Because the run-off and drainage waters in the West Coast coal mining areas are often acidic with pH < 4, which is a favourable conditions for the mobilisation of some toxic metals including Pb and Cr, both Pb and $Cr^{6+}$ may pose potential environmental concerns if they are released to the surface or into ground water in significant amounts. Therefore, it is prudent to take some measures to monitor the release of these two elements ($Cr^{6+}$ and Pb) when mining those intervals with abundant crocoite.

After combustion, most trace elements are partitioned in the bottom ash, especially in the three refractory glassy phases (Fe-oxides, Si-Al-O silicate glass, and Fe-bearing silicate glass). These elements are cemented in the aluminosilicate glass and should be difficult to mobilise unless under extreme conditions. However, most of S and Hg and a dignificant percentage of Cl, B and Cd are emitted to atmosphere by flue gas. The environmental impacts derived from the emission of these environmentally sensitive elements are far from certain because it also depends on a lot of other factors. In addition, a small portion (<10%) of the Hg is also partitioned in the fly ash fraction.

## 6.5 Limitations of This Study and Suggestions for Future Study

The author hopes the conclusions and findings of this study will serve as a foundation for better understanding the low ash nature and trace elements of Greymouth coals and provide insight into other low ash coals of similar rank or age, especially in terms of their modes of occurrence in the coal and their partitioning behaviour upon combustion. However, some limitations do exist due to shortage of funding and sample access to the Main seam. The following aspects could be pursued in future studies:

1. Although the general spatial distribution of trace elements in both the Main and E seams have been successfully established, the spatial distribution model for the Main seam needs to be validated and further refined with a more regional sampling programme to cover a wider area when sample access is improved.
2. Although the concentration of trace elements in the Greymouth coals are relatively low compared with other coals, some trace elements, including some HAPs, have been enriched to relatively high concentrations in fly ash; these elements are mainly absorbed or adsorbed onto the surface of fly-ash and are likely to be leached in large proportions particularly under acidic conditions (pH < 4). The mobility of these toxic metals from the fly ash could be further investigated in detail using sequential leaching tests or standard TCLP (toxic chemical leaching procedures).
3. Due to the limitation of access to samples of the Main seam, combustion tests were unable to be undertaken. Although both the Main and E seams are largely similar in trace elements and ash constituents, some differences do exist in terms of the proportions of individual minerals in relation to the total mineral assemblage. For example, the Main seam contains more pyrite whereas the E seam has more carbonates; this mineralogical difference may influence the combustion processes and have impacts on trace element partitioning upon combustion. Combustion tests on the Main seam coal could therefore be carried out when sampling is possible.
4. An environmental chemical study on the release of some toxic metals in the waters (surface and subsurface waters) in the Greymouth coal mining areas and in the vicinity of long-term stockpile sites should be carried out in the future.

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# Published Papers

## Papers and Statement of Contribution

The following four papers were published during the course of this study. All papers are included in the back pocket as published or reprint here with their original pagination.

Li, Z., Moore, T.A. and Weaver, S.D., 2001a. Leaching of inorganics in the Cretaceous Greymouth coal beds, South Island, New Zealand. International Journal of Coal Geology, 47 (3-4), pp. 235-253.

Li, Z., Moore, T.A., Weaver, S.D. and Finkelman, R.B., 2001b. Crocoite: an unusual mode of occurrence of lead in coal. International Journal of Coal Geology, 45 (2), pp. 289-293.

Li, Z., Moore, T.A. and Weaver, S.D. and G. Gillard, 2000. Thick and delicious: the story of Greymouth coals. Proceedings of 17$^{th}$ Annual Conference of The Society for Organic Petrology, Indiana University, Bloomington, pp. 56-58.

Li, Z., Moore, T.A. and Weaver, S.D., 1999. Mineralogy and geochemistry of Cretaceous Main Seam coal, Greymouth, West Coast, New Zealand. Proceedings of a New Zealand Energy Road Map - Vision for 2020 and 8$^{th}$ New Zealand Coal Conference, Wellington, pp. 183-199.

My contributions to all four papers were as follows:

- Leading the field work
- All laboratory work, data collection and processing, reporting and discussion
- Writing the manuscripts for submission
- Modifying and editing as required by the journal editor and final proof reading

Contributions from co-authors were as follows:

- Assisting with the field work
- General supervision, discussion and advice on early draft of manuscripts
- Assisting with editing as required by the journal editor.

# Mineralogy and Geochemistry of 'Main Seam' Coal (Cretaceous), Greymouth, New Zealand

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## ABSTRACT

This paper presents the results of mineralogical and geochemical investigations of about 80 samples from the unmined Main Seam located in the Rapahoe Sector, near Greymouth, New Zealand. The Late Cretaceous Main Seam coal has been characterised in terms of coal quality, mineralogy and geochemistry. The Main Seam coal in the study area is of high-volatile bituminous rank and had both low ash (0.5-6.7%) and sulphur (0.22-0.77%) contents. The thickness of the Main Seam in the study area is up to 21 metres.

XRD and SEM-EDAX were used to examine the low temperature ash (LTA) while XRF was used to analyse the constituents of high temperature ash. The minerals present in the LTA of coal are predominantly kaolinite, quartz and illite, together with minor to moderate amounts of carbonates, sulphides, sulfates (gypsum), and some trace minerals. Clay minerals are strongly dispersed throughout the coal, suggesting they are diagenetic in origin. Different types of pyrite and marcasite are found and are interpreted to have formed at different stages and by different origins. The major element distribution is interpreted in terms of mineralogical and ash content variations. Si and Al have strong positive correlations with ash content, whereas Fe, Mg, Mn, K and Ti have moderate positive correlations. These trends suggest a detrital origin for these components. Total sulphur shows moderate positive correlation with ash, suggesting it is mostly pyritic S. Ca, Na, have no clear correlations with ash content, suggesting their origin maybe partly associated with organic matter.

The crystallinity of clay minerals (mainly kaolinite) varies within the seam and is related to ash content. The crystallinity of illite is closely related to $K_2O$ concentration.

## Introduction

It is imperative that proper evaluation of coal is performed to assess any environmental implications from its utilisation. A key environmental aspect of coal is its inorganic constituents and how these behave upon combustion. It is the purpose of this paper to present preliminary results of the variability of the inorganic constituents of coal from the Main Seam located near Greymouth, New Zealand. More than 80 samples including coal and sediments were taken from two drill cores stored at the Greymouth core store.

The geochemistry of coal is influenced by a variety of factors such as detrital input caused by flooding, or leaching during deposition, diagenesis, burial and coalification, as well as late mineralisation [1, 2]. On the other hand, the vertical and lateral variation of major and trace elements in a coal seam is strongly controlled by various geological parameters including the nature of the source rocks, their uplift and subsidence, the flow of major river channels, climate and

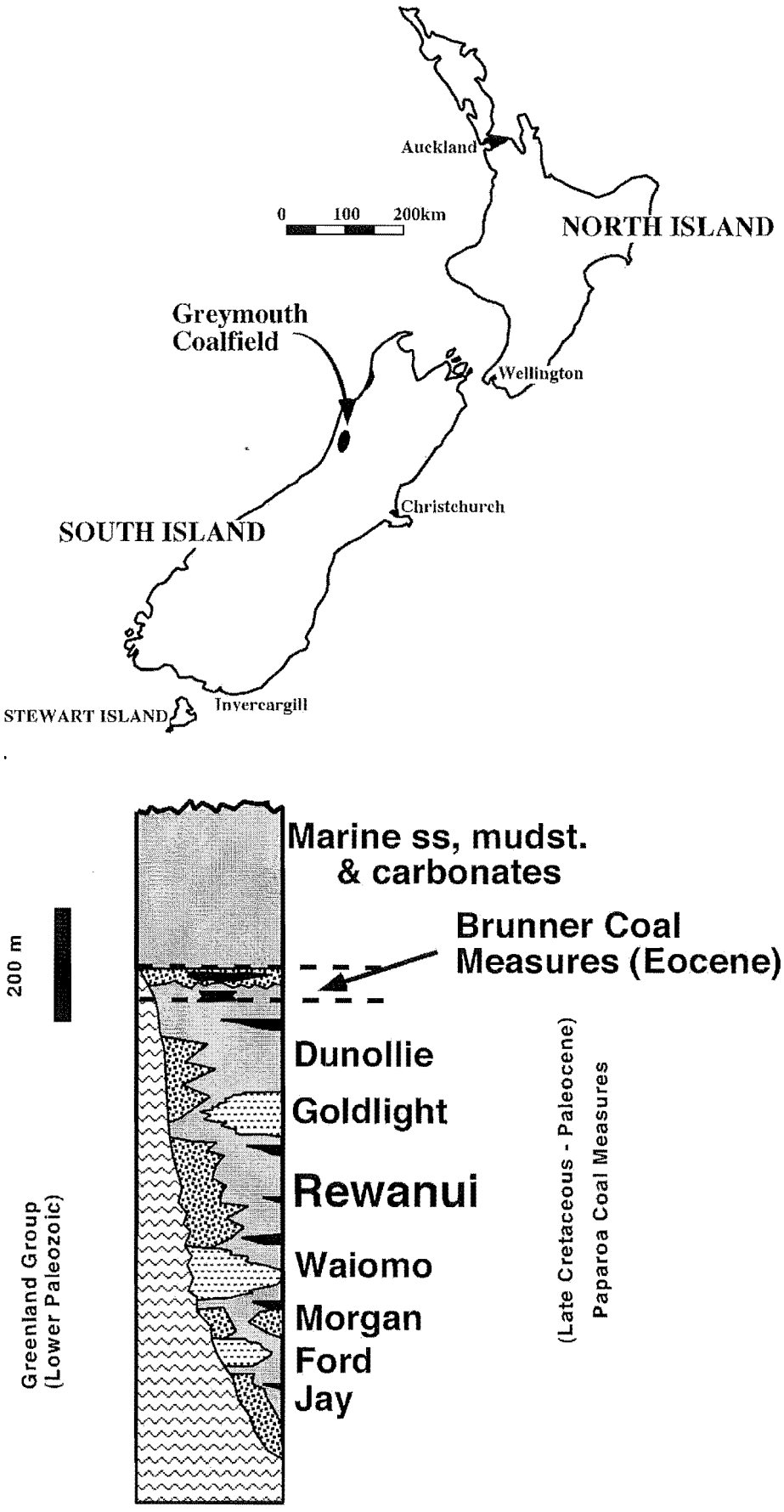


Fig. 1 New Zealand index map and generalised stratigraphic section of the study area.

hydrological conditions, bedrock geochemistry, and leaching of rocks below and above the coal seams[3]. Characterisation of these elements involves identifying coal type, abundance, and mode of occurrence.

West Coast coals are one of the most important high-rank coal resources in New Zealand, given the fact that all New Zealand's bituminous coal occurs in this area. In the West Coast region, the estimated in-ground resource is 983.5 Mt (Greymouth 543.9 Mt) whereas recoverable coal resource is 343.3 Mt (Greymouth 163.5 Mt)[4]. Total production from this region to date is 50 Mt with most coal coming from the Greymouth and Buller coalfields. Large-scale opencast mining has taken place in this region since 1944. Current annual production from the West Coast is about 1.7 Mt which is almost half of New Zealand's total annual production.

One of the most important coalfields on the West Coast is the Greymouth Coalfield. According to recent reports, Greymouth Coalfield has produced more than 30 Mt from both the Paparoa and Brunner Coal Measures since 1864. Seven underground mines are operating at present and produce 350,000 t annually. Solid Energy's Strongman Mine is the largest producer, accounting for about 85% of Greymouth production.

Because most of the coals from the Greymouth area are used for combustion, mineralogical and geochemical investigations provide important information for the evaluation of coal quality and determination of any potential problems in its subsequent utilisation.

**Previous work and Geological Setting**

Some earlier studies on West Coast coal have focused on sedimentology[5, 6], exploration and tectonics [7, 8], lithostratigraphy, palynostratigraphy and basin analysis [9, 10]. All economically important West Coast coals are restricted to either the Eocene Brunner Coal Measures or the Late Cretaceous to Early Tertiary Paparoa Coal Measures. Both groups of coal measures are present in the Greymouth coalfields. Brunner Coal Measures are Eocene and rest unconformably on either basement, mid- Cretaceous Pororari Group, or Paparoa Coal Measures. Paparoa Coal Measures span the Cretaceous-Tertiary Boundary and rest unconformably on either basement or mid-Cretaceous Pororari Group syn-rift sediments[6]. In the Greymouth Coalfield, seven formations (Fm) and members were recognised within the Late Cretaceous to Early Tertiary Paparoa Group (**Fig. 1**): Jay Fm., Ford Fm., Rewanui Coal Measure Member, Waiomo Mudstone Member and Morgan Coal Measure Member, Goldlight Fm., and Donollie Fm.[11, 6, 10]. The thick Main Seam occurs within the Rewanui Member of the Paparoa Coal Measures. The Main Seam in the study area is approximately 300 m beneath the surface and usually about 20 metre beneath the Cretaceous-Tertiary Boundary [10]. The thickness of Main Seam varies from <1 m to 30 m. For detailed geological information, readers are referred to see Newman[12], Newman[13], Newman and Newman[6], Sherwood et al[14], Moore[5] and others.

**Objectives**

The objectives of the overall study are:

1. To document the concentration of major, minor and trace elements (the interpretation of trace elements will be addressed elsewhere; here we focus on the major and minor elements).

2. To document the vertical variations in the concentrations of these elements, the distribution of selected elements in relation to ash yield and sulphur content, and to discuss their implications.
3. To determine the mineralogy of the Main Seam.
4. To determine the organic and inorganic associations, and modes of occurrence of the elements, and their possible source(s).
5. To evaluate the potential utilisation and environmental implications of the Main Seam based on the mineralogical and geochemical data.

**Sampling, sample preparation and ashing**

The Main Seam does not outcrop at the surface, therefore, samples were collected from drill core, stored at Greymouth. Because of the shortage of the availability of these coal core samples, block samples were taken based on macroscopic appearance of the coal. This sampling methodology has been used elsewhere in New Zealand[15, 16] and overseas [17, 18]. Before sampling, each core was macroscopically logged noting the appearance of sediment and charcoal layers. The coal itself was described using the proportion of vitrain bands and the lustre of the intervening attrital layers as a guide. This system for Greymouth coals is described in Ferm and Moore[19].

Every sample represents a specific portion of Main Seam in terms of lithology and depth. Sample depth represents the midpoint of a length of core representing a particular sampled interval. About 80 samples were collected including coal, associated partings, roof and floor sediments. These samples were taken from two cores, namely DH 703 and DH 755. Thirty-four samples came from unsplit thick seam (DH 703) with total thickness of 24 m (coal thickness 21.08 m). Forty-four samples came from split upper subseam (thickness of 10.87 m) and lower subseam (thickness of 8.22 m), plus associated roof (2.59 m), interburden (3.17 m), and floor rocks (1.65 m).

Coal samples were wrapped in plastic bags and crushed to small fragments by hammer, and subsplit. One subsplit was further reduced to <60 μm in a tungsten carbide swing mill for chemical analysis. The second split was crushed to <3 mm for mineralogical purposes. This part of the subset was put into an LTA for XRD mineral identification and for SEM-EDAX investigation. High temperature ash (HTA) was obtained from heating coal samples in an electrical furnace to 750°C.

**Analytical methods:**

Proximate analysis was carried out on ground whole coal. The major elements (**Table 3**) were analysed using the wavelength-dispersive X-ray fluorescence spectrometer (Philips 2400) at the University of Canterbury, Department of Geological Sciences. The major elements were determined from lithium tetraborate glass discs prepared from high temperature ash (750°C). The calibrations were based on recommended values for 39 international standard materials. All the analyses are quoted on a whole-coal basis although the major elements were analysed from high temperature ashes. Trace elements were analysed from pressed whole coal pellets using the same instrument. Some samples of ground whole coal were analysed by Instrumental Neutron Activation Analysis (INAA). Minerals in the coal were determined by XRD using subsplits of the

Table 1 Proximate analyses for the Main seam samples (as received basis)

| CRL No. | Sample No. | Moisture % | Ash % | Volatile Matter % | Fixed Carbon % | Sulphur % |
|---|---|---|---|---|---|---|
| | **coal samples** | | | | | |
| 62/722 | **755-A1** | 5.8 | 20.8 | 33.2 | 40.2 | 0.68 |
| 62/723 | **755-B1** | 6.7 | 0.7 | 42.1 | 50.5 | 0.36 |
| 62/724 | **755-C1** | 6.6 | 1.5 | 39.4 | 52.5 | 0.54 |
| 62/725 | **755-D1** | 6.5 | 1.5 | 40.6 | 51.4 | 0.45 |
| 62/726 | **755-N** | 2.9 | 43.3 | 24.0 | 29.8 | 0.89 |
| 62/727 | **755-O** | 4.9 | 41.2 | 21.8 | 32.1 | 0.22 |
| 62/728 | **755-P1** | 6.6 | 5.3 | 39.5 | 48.6 | 0.38 |
| 62/729 | **755-Q1** | 6.7 | 1.9 | 38.5 | 52.9 | 0.77 |
| 62/730 | **755-R1** | 4.5 | 3.0 | 41.4 | 51.1 | 0.68 |
| 62/731 | **755-T** | 2.2 | 60.6 | 16.9 | 20.3 | 0.95 |
| 62/732 | **703-A1** | 6.8 | 2.3 | 39.1 | 51.8 | 0.32 |
| 62/733 | **703-B1** | 6.4 | 2.2 | 39.0 | 52.4 | 0.22 |
| 62/734 | **703-C1** | 7.1 | 0.9 | 38.8 | 53.2 | 0.25 |
| 62/735 | **703-D3** | 6.3 | 0.9 | 42.8 | 50.0 | 0.34 |
| 62/736 | **703-E2** | 5.9 | 0.7 | 41.8 | 51.6 | 0.23 |
| 62/737 | **703-F2** | 5.8 | 0.7 | 43.3 | 50.2 | 0.36 |
| 62/738 | **703-G2** | 6.5 | 1.5 | 37.8 | 54.2 | 0.55 |
| 62/739 | **703-H2** | 5.2 | 1.2 | 40.7 | 52.9 | 0.48 |
| 62/740 | **703-I2** | 5.8 | 2.3 | 40.0 | 51.9 | 0.49 |
| 62/741 | **703-J2** | 5.2 | 2.9 | 38.4 | 53.5 | 0.55 |
| 62/742 | **703-K2** | 5.9 | 3.8 | 37.3 | 53.0 | 0.66 |
| 62/743 | **703-L2** | 4.9 | 3.7 | 40.9 | 50.5 | 0.70 |
| | **Inorganic partings, roof and floor rocks:** | | | | | |
| 62/749 | **755-F1** | 2.3 | 90.2 | 5.9 | 1.6 | 0.02 |
| 62/750 | **755-G** | 1.3 | 91.6 | 6.0 | 1.1 | 0.03 |
| 62/751 | **755-H2** | 1.5 | 94.3 | 4.5 | 0.0 | 0.00 |
| 62/752 | **755-I2** | 1.6 | 83.4 | 9.0 | 6.0 | 0.08 |
| 62/753 | **755-J2** | 1.2 | 93.5 | 5.5 | 0.0 | 0.00 |
| 62/754 | **755-K** | 1.7 | 87.8 | 7.5 | 3.0 | 0.06 |
| 62/755 | **755-L2** | 1.5 | 93.3 | 5.6 | 0.0 | 0.00 |
| 62/756 | **755-RF1** | 2.2 | 75.7 | 12.8 | 9.3 | 0.11 |
| 62/757 | **755-RF3** | 2.9 | 67.5 | 15.1 | 14.5 | 0.20 |
| 62/758 | **755-FL1** | 0.9 | 95.9 | 3.3 | 0.0 | 0.00 |
| 62/759 | **755-FL3** | 1.4 | 90.4 | 6.5 | 1.7 | 0.01 |
| 62/760 | **703-RF1** | 1.5 | 93.2 | 5.1 | 0.2 | 0.01 |
| 62/761 | **703-RF2** | 1.3 | 95.3 | 3.6 | 0.0 | 0.00 |
| 62/762 | **703-RF3** | 1.6 | 78.0 | 20.5 | 0.0 | 0.27 |
| 62/763 | **703-FL1** | 2.3 | 56.7 | 19.9 | 21.1 | 0.51 |
| 62/764 | **703-FL2** | 1.5 | 90.8 | 6.3 | 1.4 | 0.05 |
| 62/765 | **703-FL3** | 1.9 | 87.1 | 7.5 | 3.5 | 0.22 |

LTA. Textures and banding characteristics were examined by microscope on polished sections; SEM-EDAX was used for mineralogical investigation and determination of chemical composition on specific grains or areas on polished sections and pellets.

**Results and Discussions**

1. Coal Quality and Petrographic Characterisation

The proximate analysis results are given in **Table 1**. Volatile matter content (exclusive of partings, roof and floor) varies between 33.2 to 42.8%. On the basis of volatile matter, these coals are classified as high volatile A to B bituminous in rank[20]. The ash yield and sulphur content of the Main Seam (exclusive of dirty coal, partings, roof and floor) varies between 0.5 to 6.7 (wt%, air dry basis) and 0.22 to 0.77(wt%), respectively. Maceral components in the coal seam comprise vitrinite (>90%, and in some case up to 97%), liptinite <2%, and inertinite < 5%.

The predominance of vitrinite suggests an extremely high degree of preservation of decaying plant material in the swamp. The inertinite maceral predominantly present in the samples examined is fusinite (pyrofusinite), usually with well-preserved distinctive cellular structure, such as "sieve structures" [21]. Some of the cell voids are filled with minerals, like pyrite and clay.

2. Mineralogy

The inorganic components in coal occur either as discrete mineral grains or are bound organically. The chemical elements in coal are mostly associated with the mineral phases in the form of aluminosilicates, carbonates, sulphates[22, 1], sulphides and oxides. Minerals generally found within coal are listed in **Table 2**. In the Main Seam, the predominant minerals are quartz and clay minerals, including kaolinite, illite, and mixed-layer clay. Other commonly occurring minerals include pyrite, marcasite, tschermigite, calcite, siderite, ankerite, gypsum, rutile. All other minerals are rare. The mineralogy shows some variations within the seam, varies with burial depth and microlithological type.

Table 2. Minerals present in Main Seam:

| |
|---|
| Clay minerals: kaolinite, illite, interstratified phyllosilicate (smectite). |
| Sulphides: pyrite, marcasite, sphalerite, |
| Carbonates: calcite, siderite, ankerite, |
| Sulphates: gypsum, anhydrite, tschermigite, alunogen. |
| Oxides: quartz, chert, haematite, magnetite, goethite (FeOOH) |
| Other trace minerals: muscovite, biotite, halite, apatite, $Al(OH)_3$, sylvite (KCl), monozite, anglesite, rutile, zircon, Pb-Cr compound mineral (Crocoite) |

2.1. Clay minerals and their crystallinity.

Clays, mainly kaolinite, generally comprise ca. 80% of the minerals present in Main Seam, although in few cases, quartz (up to 50%) dominates in the lower part of the coal seam adjacent to dirty coal or partings. Kaolinite occurs in at least three distinct forms: 1) As finely-crystalline aggregates, up to a few microns in size, intimately disseminated in organic matter. Interestingly, sometimes clay and coal can be seen as complex intergrowths. This finely-crystalline syngenetic clay is thought to have formed from mineralised solutions percolating through the coal. 2). A

small amount of kaolinite is also present as plates (a few cm), and in cleat-or fracture-fillings. We interpret this as an epigenetic clay. Under SEM, kaolinite consists of hexagonal platelets and curved stacks of plates. 3). The third form of clay is associated with inertinite macerals and is admixed with sulphide, mainly pyrite, and sometimes intergrown with pyrite or carbonates. This kind of clay may be syngenetic in origin and associated with fusinite.

Illite is only present in an appreciable amount (XRD detectable at >5%) in the lowest part of the split lower seam and dirty coal. There are two possibilities, namely paucity of K and/or the poor crystallinity of illite, leading to the absence of detectable illite in most parts of the seam. The acidity (pH) also affects the crystallisation of illite. Inter-layer clays, such as smectite are not commonly seen, but are sometimes associated with fusinite.

The crystallinity of clay minerals varies slightly within the seam and between seams. An attempt was made to study the crystallinity of clay minerals using methods described by Murray and Lyons[23] and Dimanche et al[24], by comparing the diffractogram patterns of random powder preparations. The crystallinity reflects the layer stacking disorder. However, the crystallinity of kaolinite in the Main Seam shows only slight differences. A general trend of crystallinity was only obtained for the thick seam in DH 703 (24m thickness). The crystallinity of clay minerals (mainly kaolinite) tends to improve downward from the roof or upward from the floor of the coal seam. The crystallinity of illite is closely related to $K_2O$ concentration.

2.2 Sulphides

Pyrite occurs as three different forms in the Main Seam:

**A).** Epigenetic pyrite has been observed as occurring locally within the coal seam, especially in the split lower seam. This pyrite apparently is within the cleat network of the coal. It usually occurs as single discrete euhedral grains, or coalesced to form masses and sheets which coat the face of the cleats, or as infillings deposited within cleats, cracks, or fractures, from tens of microns to several centimetres in size. Some workers termed this "massive" or "cleat" pyrite [22, 25]. This kind of pyrite is interpreted as epigenetic pyrite and formed from mineralised solution after peat deposition. The pyrite is usually relatively clean, although in some cases has micro-fractures, admixed with another phase or contains inclusions, commonly accompanied by clay minerals and/or quartz. Smyth[26] pointed out some primary siderite can transform into pyrite by interaction with $H_2S$-containing solutions. The formation of epigenetic pyrite is dependent primarily on the availability of reduced S, dissolved cations (ferrous iron) and a suitable site for deposition (i.e. cleat).

**B).** Syngenetic pyrite is formed during the peat stage. It is frequently extremely fine-grained and is disseminated throughout the coal organic matter. This kind of pyrite maybe formed during the coalification stage as a diagenetic mineral.

**C).** Massive pyrite occurs associated with inertinite, either as fusinite cell-fillings or as impregnations of fusinite or semifusinite with pyrite (replacing original plant tissue). This type of pyrite replaces plant tissues with components (e.g. Fe or S) from percolating solutions or from plant material itself.

2.3 Carbonate and Sulphate

Most carbonates occur as infilling minerals within cleats or at maceral boundaries, and are most likely to occur within or associated with inertinite. They are especially prevalent in dirty coal from the split lower seam section and in the section near the floor (e.g. samples 755-T and 755-N respectively).

Calcite and siderite occur mainly as euhedral grains, pseudomorphs, or massive in the highly carbonaceous dirty coal or the associated partings. Most of the siderite appears to be associated with inertinite but in some cases does occur as discrete grains dispersed in vitrinite. Most calcite was found as euhedral crystals in vitrinite. Ankerite tends to occur in dirty dull coal close to the mudstone sediments.

Gypsum occurs as elongate euhedral crystals in the vitrinite matrix, and possibly formed after coalification, or even later, as a secondary mineral. However, the formation of gypsum during the storage of coal can not be ruled out. Dehydrate occurs as a fibrous assemblage associated with vitrinite.

Ammonium-bearing tschermigite was detected by XRD in the LTA of some coal samples. It may be derived as a decomposition product of nitrogen compounds present in the organic matter. Ward[27] also noted this mineral in the LTA of leached Thailand coal samples, and in the LTA of leached South Australian low rank coal samples. Ward[27] suspected the $NH_4^+$ in Australian samples was a residue from the ammonium acetate solution which he used for leaching his samples.

2.4 Oxides

Quartz is one of the most important minerals in the Main Seam, usually present as two different forms. 1). As euhedral, lenses or lensoid, subangular to semi-rounded grains, sometimes occurring as clusters parallelled to bedding. Some quartz grains accommodate inclusions, such as zircon. This type of quartz was most likely brought to the swamp during the peat accumulation and is of a clastic origin. 2). Quartz is also present as finely-crystalline discrete grains (less than 5 μm) intimately dispersed in the organic matter. Andrejeko et al.[29] point out that the interior of some modern peat deposits are substantial reservoirs of amorphous silica, derived from the degradation of diatoms, sponge spicules and siliceous phytoliths associated with the organic matter. This silica appears to be mobile under certain conditions within the peat-forming environment. This syngenetic quartz may be the result of precipitation or crystallisation of dissolved silica solution either due to weathering of feldspars or micas, or from a mobile leaching solution.

2.5 Other minor and trace minerals.

Rutile crystals are commonly seen in clay minerals in the Main Seam, mostly as inclusions. Rutile or anatase seen as discrete grains were detected under SEM-EDAX. Halite and sylvite grains are sometimes found as fine grains dispersed in organic matter, and may indicate a relatively low ground water level or the presence of mobile solutions leaching through the coal.

Table 3 Major and minor element analyses for Main seam (quoted as on whole coal basis, in %)

| Lab. No. | Field no. | Depth | VBD%* | Ash | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $S_{tot}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 31247 | **703-A1** | 322.2 | >20 | 1.60 | 1.652 | 0.033 | 0.397 | 0.027 | 0.023 | 0.009 | 0.036 | 0.047 | 0.009 | 0.001 | 0.32 |
| 31249 | **703-B1** | 323.5 | <20 | 2.20 | 1.833 | 0.030 | 0.190 | 0.030 | 0.022 | 0.007 | 0.030 | 0.038 | 0.004 | 0.001 | 0.22 |
| 31251 | **703-C1** | 324.9 | NBD* | 0.90 | 0.559 | 0.012 | 0.195 | 0.027 | 0.000 | 0.005 | 0.024 | 0.029 | 0.003 | 0.000 | 0.25 |
| 31254 | **703-D2** | 326.8 | <20 | 0.58 | 0.300 | 0.007 | 0.152 | 0.026 | 0.000 | 0.005 | 0.021 | 0.022 | 0.002 | 0.000 | 0.34 |
| 31259 | **703-F2** | 332.6 | <20 | 0.79 | 0.284 | 0.008 | 0.173 | 0.195 | 0.000 | 0.006 | 0.029 | 0.009 | 0.002 | 0.000 | 0.36 |
| 31261 | **703-G1** | 337.2 | >20 | 2.68 | 1.795 | 0.030 | 0.355 | 0.377 | 0.027 | 0.005 | 0.026 | 0.028 | 0.004 | 0.001 | 0.55 |
| 31264 | **703-H2** | 339.2 | <20 | 1.43 | 0.571 | 0.010 | 0.384 | 0.310 | 0.014 | 0.005 | 0.025 | 0.024 | 0.004 | 0.001 | 0.48 |
| 31266 | **703-I1** | 340.3 | >20 | 1.59 | 1.123 | 0.032 | 0.247 | 0.115 | 0.016 | 0.003 | 0.014 | 0.026 | 0.003 | 0.001 | 0.49 |
| 31268 | **703-J1** | 340.8 | <20 | 2.65 | 1.618 | 0.029 | 0.682 | 0.202 | 0.027 | 0.006 | 0.026 | 0.025 | 0.006 | 0.001 | 0.55 |
| 31272 | **703-K2** | 342.1 | >20 | 2.76 | 1.561 | 0.089 | 0.513 | 0.399 | 0.028 | 0.006 | 0.070 | 0.030 | 0.007 | 0.002 | 0.66 |
| 31274 | **703-L2** | 342.9 | DBD*<20 | 3.74 | 2.025 | 0.053 | 1.121 | 0.373 | 0.037 | 0.016 | 0.023 | 0.028 | 0.049 | 0.003 | 0.70 |
| 31229 | **755-A2** | 332.6 | >20 | 1.10 | 0.692 | 0.013 | 0.101 | 0.080 | 0.000 | 0.007 | 0.067 | 0.030 | 0.004 | 0.001 | 0.68 |
| 31232 | **755-B3** | 339.7 | <20 | 1.41 | 0.823 | 0.017 | 0.279 | 0.151 | 0.000 | 0.006 | 0.025 | 0.030 | 0.004 | 0.001 | 0.36 |
| 31236 | **755-D2** | 341.9 | <20 | 1.58 | 0.916 | 0.019 | 0.368 | 0.158 | 0.000 | 0.006 | 0.028 | 0.022 | 0.004 | 0.001 | 0.45 |
| | **Partings** | | | | | | | | | | | | | | |
| 31239 | **755-P2** | 348 | <20 | 1.39 | 0.798 | 0.025 | 0.284 | 0.152 | 0.000 | 0.007 | 0.027 | 0.023 | 0.004 | 0.001 | 0.38 |
| 31242 | **755-Q2** | 350.5 | >20 | 3.02 | 1.368 | 0.021 | 0.586 | 0.837 | 0.001 | 0.009 | 0.030 | 0.036 | 0.010 | 0.001 | 0.77 |
| 31244 | **755-R2** | 351.9 | <20 | 6.70 | 4.740 | 0.091 | 0.704 | 1.030 | 0.001 | 0.009 | 0.026 | 0.019 | 0.012 | 0.002 | 0.68 |
| 31246 | **755-S** | 352.9 | >20 | 5.11 | 3.421 | 0.126 | 1.249 | 0.181 | 0.051 | 0.013 | 0.026 | 0.044 | 0.020 | 0.004 | 0.50 |
| 31225 | **755-N** | 755-N | dirty coal | 43.30 | 27.898 | 0.355 | 5.421 | 3.100 | 0.022 | 1.390 | 2.966 | 0.048 | 1.165 | 0.013 | 0.89 |
| 31226 | **755-O** | 755-O | DBD>20 | 41.20 | 34.575 | 0.400 | 4.227 | 0.519 | 0.412 | 0.247 | 0.037 | 0.066 | 0.993 | 0.012 | 0.22 |
| 31227 | **755-T** | 755-T | dirty coal | 60.60 | 41.000 | 0.588 | 12.702 | 2.545 | 0.006 | 0.661 | 0.036 | 0.097 | 2.436 | 0.024 | 0.95 |

* VBD = vitrinite banded, DBD = dull banded, NBD = non-banded, $S_{tot}$ = toal sulphur

3. Geochemistry, elemental variations and their mobility

With a few exceptions, most elements within the Main Seam are present in minor or trace amounts. The concentration of elements on a whole coal basis, is usually categorised as major (>0.5%), minor (0.02 to 0.5%), or trace (<0.02% or 200 ppm and lower). The major and minor element analyses are given in **Table 3**. It is noted that some elements that are normally considered majors have fallen into minor or even trace element category because of the exceptionally low ash content of these coal samples.

3.1 Comparison of vertical variation of selected elements and ash content between DH755 and DH 703.

3.1.1 Thick unsplit seam: DH703 (coal thickness=21.08m).

A). Ash and $SiO_2$. The concentrations of $SiO_2$ and ash have almost the same trend in variation. The correlation coefficient R=0.99 between $SiO_2$ and ash content suggests that $SiO_2$ is the controlling factor for the ash proportion. The ash and $SiO_2$ content decrease dramatically from both the roof and floor toward the central portion of the coal seam (**Fig. 2A**) where both are exceptionally low. The only exception is in the sampling interval 703-G (337-338 m). Within this interval, the content of all the elements, especially Si, Al and Fe is significantly elevated. Two possible processes could explain this: a). An abrupt change of environmental conditions (e.g. pH, Eh) favoured the precipitation of silica in the swamp during that period of time. b). Some unusual process (flooding or subsidence, etc.) occurred to let the swamp gain access to inorganic input before extensive leaching occurred. The former process seems more likely. It is interesting to note that this inteveral is most likely correlated to the split seen in DH755.

B). $Fe_2O_3$ and Total Sulphur ($S_{tot}$). $Fe_2O_3$ and $S_{tot}$ show very similar vertical distribution trends in DH703 (see **Fig. 2A**). The correlation coefficient between $Fe_2O_3$ and $S_{tot}$ is R=0.72. This confirms that iron sulphides (mainly pyrite) control the $Fe_2O_3$ content in the Main Seam, and is consistent with observations from mineralogical investigations. Both contents of Fe and $S_{tot}$ increase with depth. $Al_2O_3$ shows a similar trend to that of $Fe_2O_3$, suggesting a connection between them. The mineralogical observation that in some cases, clay and pyrite coexist or are intergrown, especially within inertinite macerals or at boundaries between vitrinite and inertinite, is further evidence of $Al_2O_3$/ $Fe_2O_3$ correlation. The correlation coefficient between $Fe_2O_3$and $Al_2O_3$ is R=0.81

C). $Al_2O_3$, $TiO_2$, $K_2O$, MnO. The abundance of these 4 elements has a similar trend to that of Silica (**Fig. 2A**). The cental portion of the coal has the lowest content of all four components. The only exception occurred near the floor, where the $TiO_2$ fluctuated dramatically, probably due to the increasing influence of carbonates from floor rocks. Obviously this group of elements are closely related with the clay minerals kaolinite and illite. The inter-element correlations (**Fig. 3**) also support this theory, with inter-element correlation coefficients being 0.99, 0.96, 0.95, 0.71 for $Al_2O_3$ and $K_2O$, $TiO_2$ and $Al_2O_3$, $TiO_2$and $K_2O$, MnO and $Al_2O_3$, respectively. The mineralogical investigation shows rutile ($TiO_2$) as common inclusions in clay; Mn may also be associated with clay. Although we encountered some sylvite (KCl) grains in trace amounts during SEM examination, the very strong positive correlation of Mn with Al and Si suggests that the role of sylvite is insignificant.

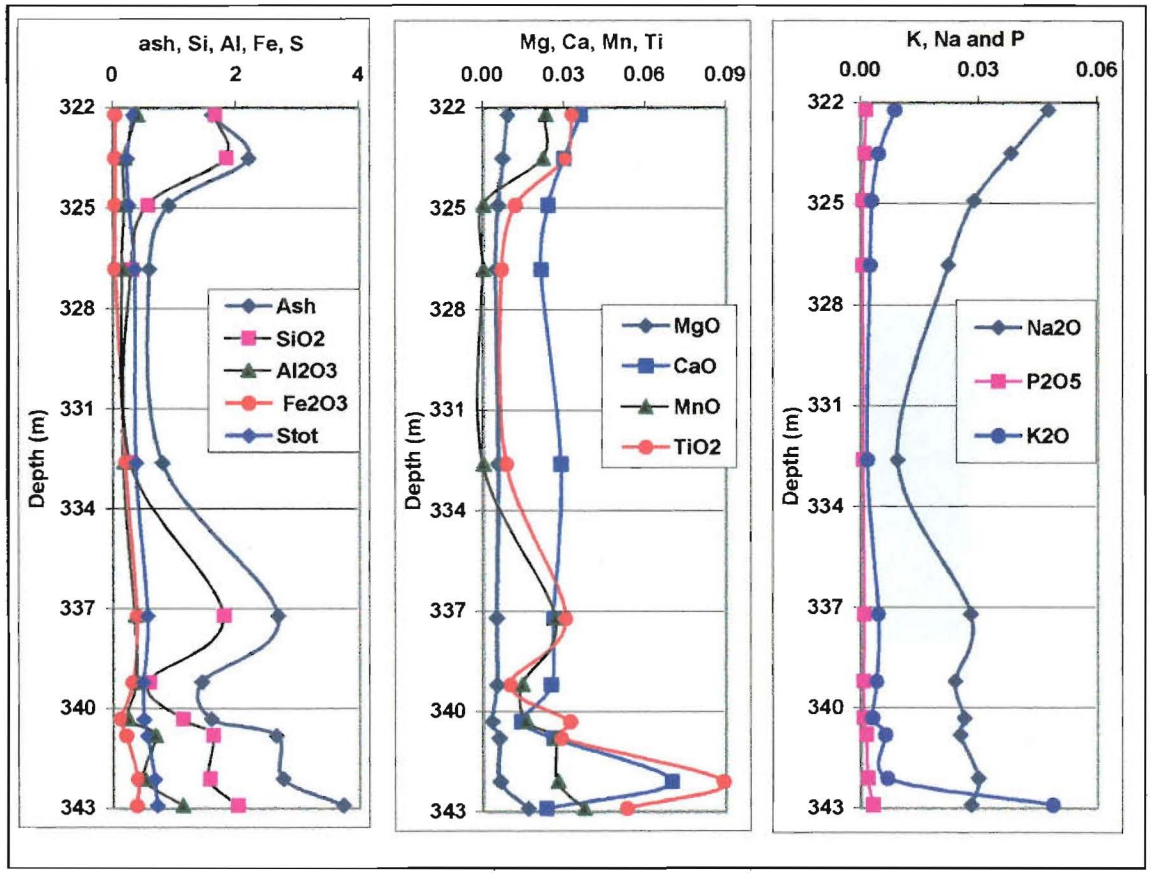


Fig. 2A Ash yield(%) and major element oxides (%) vertical distribution in DH 703

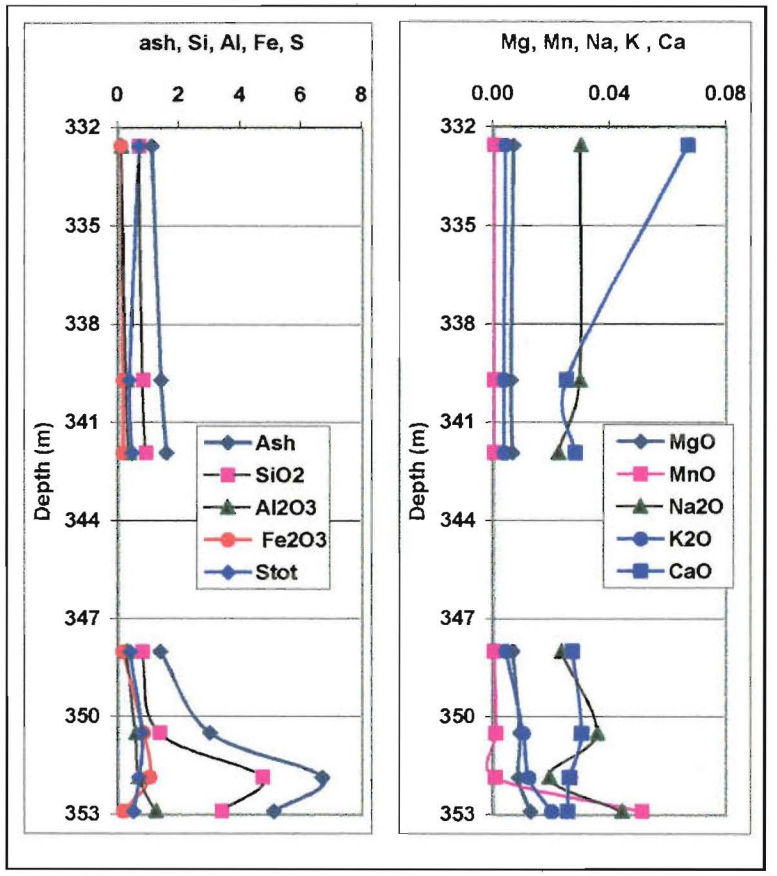


Fig. 2B Ash yield (%) and major element oxides (%) vertical distribution in DH 755.

D). CaO, MgO, $Na_2O$, $P_2O_5$.
CaO, MgO, $P_2O_5$ concentrations are quite constant right down through most of the thick coal seam except close to the floor where MgO increases sharply and CaO increases sharply then decrease dramatically (**Fig.2A**). The variation of CaO and MgO content near the floor is probably due to the increased influence of carbonates in floor rocks.

$Na_2O$ has its highest concentration in the top portion of the seam, and that could be explained as bioaccumulation by plants. Shotyk[30] found that there was much higher K and Na content in the surface peat because of the plant bioaccumulation in the vertical peat profiles of three Canadian peat bogs. In the Main Seam $Na_2O$ decreases from 474 ppm near the roof downward to the centre part of the seam, until ~333 m where it reaches its lowest level (92 ppm), between 333 m and 337 m it increases from 100 to 280 ppm, then it fluctuates between 250 to 300 ppm. The content of $Na_2O$ in the cental portion of the seam is 3 to 5 times lower than that of coal near the floor and roof. The $K_2O$ concentration at the same portion is 32 times lower than that near the floor. The content of $Al_2O_3$, $TiO_2$, MnO is also at the lowest level within this interval. All this evidence of elemental mobility suggests that intensive leaching occurred, or that the paleo-water table had been fluctuating within this seam interval and had flushed away most elements.

3.1.2 Vertical variation of elements in splitted main seam DH755.
The Main Seam in DH755 occurs as two plys, or splits, with coal thicknesses of 10.87 m (upper split) and 8.22 m (lower split). Between the upper and lower seams are 3.17 m of partings comprising grey, root penetrated mudstone, sandstone and claystone. It should be pointed out that the lower seam includes 0.57m of dirty coal at its top (755-N and 755-O, from depth 345.63 to 345.80 m, ash 43.3 and 41.2% respectively) and 0.75 m of dirty coal near the floor (755-T, depth from353.10 to 353.85 m, 60.6% ash). All the element concentrations are much higher within these dirty coal layers. The following discussion on vertical distribution trends has excluded this dirty coal, roof and floor rock samples. The other notable fact is that almost all elements have higher concentrations in the lower seam than that in the upper seam (**Fig. 2B**).

A). Ash, $SiO_2$, $Al_2O_3$, $Fe_2O_3$. Unlike the trend seen in DH703, all four components in both the upper and lower seam clearly increase with depth (**Fig. 2B**), except near the floor in the lower seam seen in 755-S (depth 352.9m, adjacent to the dirty coal floor) where ash, $SiO_2$ and $Fe_2O_3$ decrease sharply, whereas Al, K and Na increase substantially. This suggests pH increases due to the increase of alkali elements. Illite has crystallised with kaolinite. The pH and the formation of illite perhaps affected the precipitation of silica and pyrite, and decreased the ash content. The vertical variation curves for $SiO_2$, $Fe_2O_3$ and ash content (**Fig. 2B**) look exactly the same in both upper and lower seam. This suggests that in split Main Seam Si (in the form of quartz and clay) is still the controlling factor of the ash content. Fe also seems to play a more important role in controlling ash content, more than it does in DH703.

B). $TiO_2$, MnO, MgO, $K_2O$
In the upper seam, these components tend to be constant in low concentrations or vary over a very narrow range.

In the lower seam, all these components appear to increase downwards (**Fig. 2B**). This is especially the case for $K_2O$ and $TiO_2$, which reflect the variation of $Al_2O_3$. These increases are closely associated with clay minerals.

C). CaO and $Na_2O$.
CaO decreases from the top to the central part of the upper seam, then tends to be unchanged or changes little right down through the entire lower seam (**Fig. 2B**). $Na_2O$ decreases with depth in the upper seam, but fluctuates in the lower seam.

4. Mode of occurrence
Based on the mineralogical study and the geochemistry of major element analyses, we interpret the modes of occurrence of the elements as follows:

A). Si, Al, K, Ti
Each of these four elements are strongly correlated with the ash in both DH703 and DH755. The minerals relating to these elements are predominantly quartz and clays including kaolinite, illite and mixed layer clay. Tschermigite and alunogen do occur but only in very few samples and their concentrations are not significant. Rutile is commonly seen as discrete grains or inclusions associated with clay and is the main host for Ti. The inter-element correlation study (**Fig. 3**) also shows strong positive correlations with R=0.92 for Si and Al, 0.99 for Al and K, 0.96 for K and Ti, 0.95 for Al and Ti. It is therefore concluded that: quartz and clay minerals are responsible for Si; and kaolinite and illite for Al and K. Although we encountered a few fine-grained discrete sylvite grains in trace amounts under SEM-EDAX, the very strong positive correlation between K and Al, and K and Si confirms that the contribution of K from sylvite is not significant. Some sulphates are responsible for a small proportion of Al.

B). Fe, S
Total sulphur has a positive correlation with ash content (**Fig. 4**). This suggests that S occurs mainly inorganically either as sulphides or sulphates. The minerals responsible for these two elements are iron sulphides, mainly pyrite, in some cases associated with marcasite, siderite, ankerite and sulphates (gypsum, dehydrate). It was found that S occurs mainly as pyritic S and that sulphides are the major contributor of S compared with sulphates and siderite (excluding partings, roof and floor rocks samples). The vertical variation curves of Fe and S also follow the same pattern (**Figs. 2A and 2B**). The almost linear positive correlation between Fe and total S (**Fig. 3**) supports the above conclusion. It cannot be ruled out, however, that a small amount of S is associated with organic matter.

C). Mn, Ca, Mg, Na, P
We concluded that carbonates (mainly calcite, ankerite) and gypsum are responsible for Ca. The positive correlation (**Fig. 3**) between Ca and Mg also suggests carbonates control the later. CaO shows no clear correlation with ash content. This may indicate that some CaO is associated with organic matter.

The behaviour of Mn and K and Al are surprisingly similar. Mn shows positive correlation with Al and K (**Fig. 3**). This suggests Mn may be present within the clay mineral illite as fine

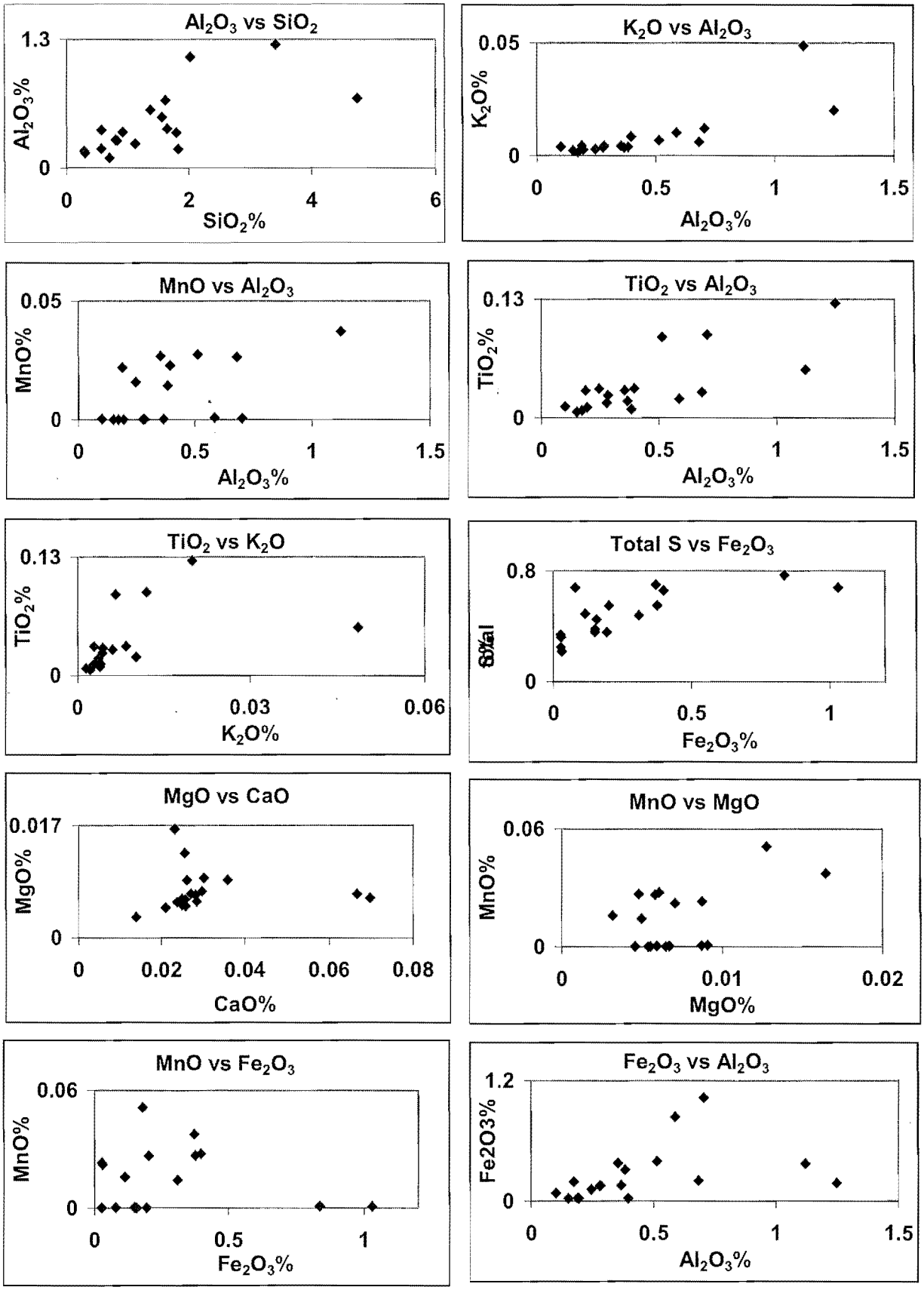


Fig. 3 Inter-elemental correlations within the Main seam coal (excluding dirty coal and partings)

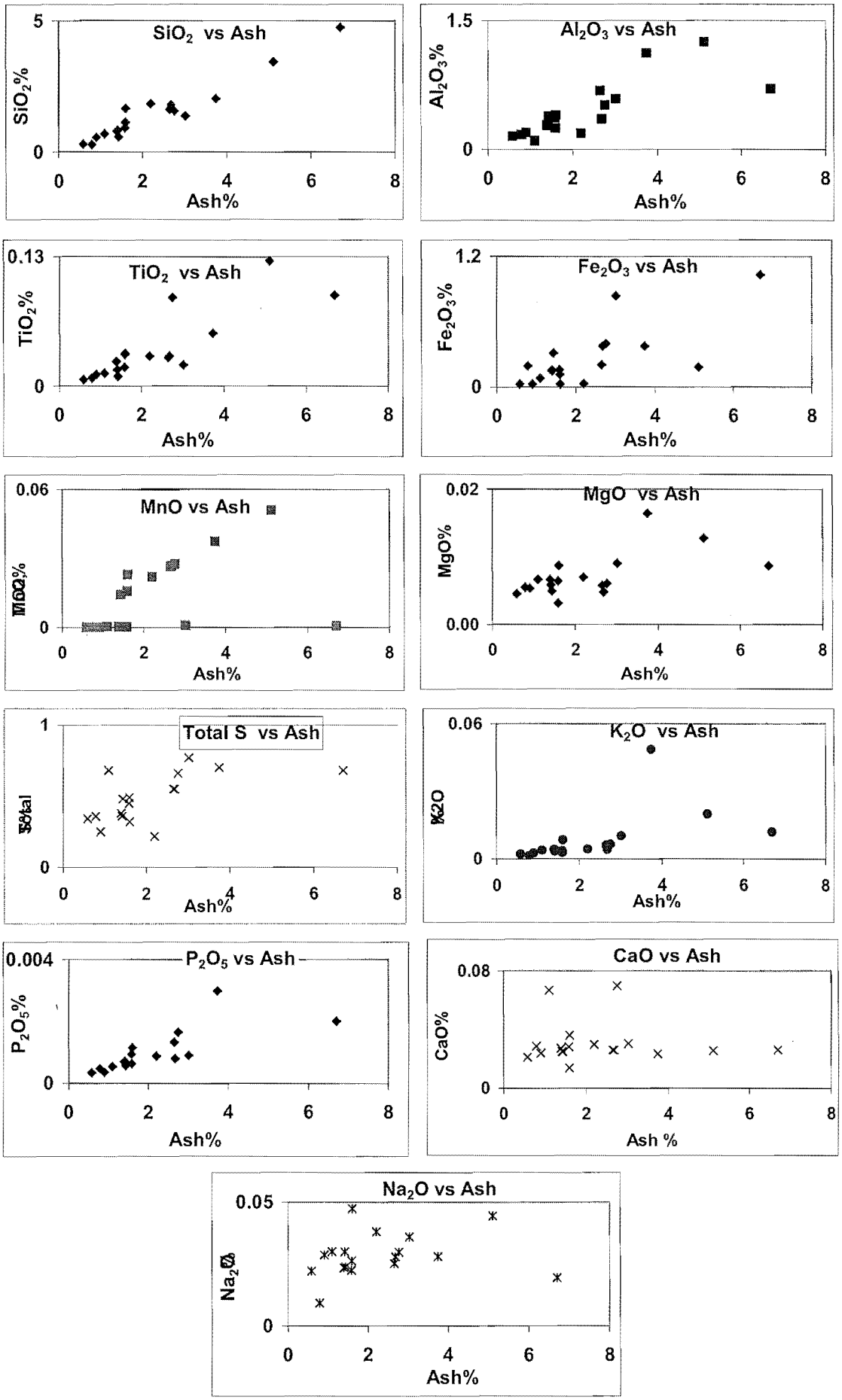


Fig. 4 Major elements vs ash contents within the Main seam coal

inclusions. The lack of clear correlations between Mn and Mg, Mn and Ca, and Mn and Fe (**Fig. 3**), decreases the possibility of Mn occurring in carbonates. The factors controlling Mn distribution are still uncertain.

$Na_2O$ shows a positive correlation with ash content (**Fig. 4**), although it is not a strong correlation. A few halite grains were encountered under SEM-EDAX, but it may not be the only occurrence of Na. The other possibility is as a substitution of K associated with illite. $P_2O_5$ shows positive correlation with ash and it may occur as phosphate (e.g. apatite).

**Conclusions:**

1. The extremely low-ash in such a thick high-rank coal seam suggests the Main Seam formed under very special conditions, namely a restricted inorganic input and/or that it experienced extensive leaching.
2. The concentration of major and minor elements tends generally to increase with depth within the seam.
3. The content of $SiO_2$ is the controlling factor for ash content, although $Al_2O_3$ and $Fe_2O_3$ also make significant contributions.
4. The modes of occurrence of most of major elements have been documented and they occur mostly as commonly found minerals, e.g quartz and clay minerals.

**Acknowledgments**

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# Thick and delicious: the story of the low ash Greymouth coal seams

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**Abstract**

The Late Cretaceous age coal seams on the West Coast of the South Island in New Zealand are important and anomalous. These coals represent approximately 10% of New Zealand's total coal production and with the start of new mines, this figure will double in the next couple of years.

In order to understand the geological and geochemical factors that controlled coal quality and seam geometry in this region, two seams were investigated in detail with respect to coal quality and petrography. About 160 samples including coal, inorganic partings, roof and floor rocks, were collected. These samples came from a combination of boreholes, underground mine and opencast mine sites from two coal beds (the "E Seam" and "Main Seam") located in the Rapahoe Sector, near Greymouth, New Zealand. The thickness of Main Seam ranges from 1 m up to more than 30 m (typically 10 to 20m), whereas E Seam ranges from <1 m to 14 m. The thickness of coal seams varies across the basin, sometimes abruptly over short distances.

What makes the Greymouth coal seams anomalous, and therefore interesting, are their extremely low ash nature. For example, the two seams studied generally have ash yields of 1% to 3%. Other Cretaceous coals worldwide have ash yields ranging from 10% to 25% (McCabe & Parrish, 1992). In fact, most coals irrespective of age have ash yields between 5 to 10%. What is also notable is that even peat has ash yields generally in the range of 1% to 5% (Neuzil, et al., 1993, Ruppert, et al., 1993). How therefore can a coal bed have even less inorganic material than the starting materials?

Two hypotheses have been formulated here to explain the low ash nature of the Greymouth coal seams: 1) The inorganic material in the coal seams have been leached sometime after burial, or 2) Greymouth coal seams represent an unusual type of coal-forming regime, possibly with different vegetation, accumulation dynamics, depositional environment parameters and/or coalification scheme.

In order to understand the way in which the ash yield is distributed in the Greymouth coal seams, two seams were investigated in detail. Fig 1 gives a typical ash profile of the Main Seam in drill hole 703. Although ash yields are around 2% at both the top and the bottom of the seam, the ash yield decreases dramatically toward the centre of the seam where it is as low as 0.5%. This profile is seen in all eight of the other seam profiles analysed.

Ash mineralogy was also investigated to help understand the low ash nature of the coal seam. It was found that the composition was relatively simple, consisting mostly of clays (kaolinite, illite, smectite, etc.) and quartz. Pyrite was also commonly seen in Main Seam whereas carbonates (siderite, calcite, ankerite) were common in E Seam, along with trace of sulphates and other silicates (Li et al, 1999).

Organic and inorganic petrography shows some interesting observations. These are: the presence of void-filling bitumen, the low inertinite content, and the etched nature of quartz

grain boundaries. The maceral composition of both seams is predominately vitrinite (85% to 95%, on mineral matter free basis), with some liptinite (1-5%), and low inertinite (2% to 10%). Most of the liptinite is sporinite plus minor cutinite, and rare traces of alginite. Interestingly, bitumen is usually present either within vitrinite matrix or inertinite (mostly semifusinite). However, wherever it occurs, it infills cavities (like cell lumens) associated with microcleats connected to other larger cleats or fracture networks, or adjacent to major cleat and mineral matter rich layers.

In order to understand how the low ash Greymouth coal seams occur, the depositional settings have also been investigated. The two seams are thought to have been deposited on floodplains associated with fluvial and lacustrine sequences (Bowman, 1982, Sherwood, et al., 1992, Newman & Newman, 1992, Moore, 1996). Compared with the depositional settings of other Cretaceous coals, the depositional settings in Greymouth are not unusual. The low sulphur content (Fig. 1) and the absence of marine-related minerals supports the conclusion that the coals formed within a fresh water depositional environment. Vegetation which formed the Greymouth coals (mostly Podocarps; Moore, 1996) was in no respect unusual. Overall, these data do not set apart the Greymouth coal seams from other coals worldwide.

Do therefore the physical and chemical properties of Greymouth coals give us any clue for explaining their low ash yield nature? In fact, some physical and chemical evidence suggests that leaching of inorganic material has occurred. Evidence for this is: 1) Bitumen is defined as a material containing mainly heavy heteroaromatic molecules and interpreted as a product during the late diagenetic stage before oil-generation (Mastalerz et al., 2000). Recently, solid bitumen in coals has also been suggested to be an important source of gas in Bowen Basin coals over a wide range of maturation levels (Glikson et al., 1999). It is known that bitumen is usually associated with gas or oil generation and movement in the coalbed (Mastalerz, pers. Comm., 2000), and the presence of bitumen may indicate that liquid hydrocarbon generated by coal migrated through the cleats or fractures in the coal seams. The association of bitumen with minerals suggests that mineral-bearing fluids accompanied liquid hydrocarbons generated by the coal and migrated through the coal seam. Perhaps, while some minerals were trapped in the coal (some semifusinite and fusinite have been filled with minerals like clay, pyrite, and small quartz grains), some of them were removed during this phase, thus helping to lower the overall ash yield of the Greymouth coal seams. 2). It is known that vitrinite and inertinite are principally derived from the same source material (such as wood, leaf, root tissue, etc.). However, if the plant material has been oxidised either biochemically or by fire or desiccation early in its diagenetic history, more inertinite should be present. The low concentration of the inertinite and extremely high vititrinite content may suggest that the climate was wet and the water tables high during the peat accumulating stage. This situation would favour the mineralised (chemical) solution or ground water percolating activities through the peat. Therefore, the seams were formed and developed under relatively reduced conditions and were not exposed to oxidising conditions for most of the time following the peat accumulation. 3). The etched grain boundaries of quartz suggests that there has been some secondary dissolution by fluids.

In conclusion, the depositional settings of Greymouth coal beds are not unusual compared with other Cretaceous coals from around the world. However, some physical and chemical evidence (such as the presence of bitumen, low abundance of inertinite, the etched grain boundaries in quartz) support the conclusion that a leaching process and/or percolating processes may have taken place at some stage in Greymouth coal beds. The leaching and/or

solution percolating activities clearly indicate the inorganics may have been mobilised, and some of them have been removed from the coal seams by this process. The leaching and/or percolating processes are believed to be a significant factor which attributed to the low ash nature of the coals. More work is needed to evaluate the significance of depositional settings of Greymouth coal beds and to examine the inorganic sources and their mobility.

**Keywords:** Cretaceous, bituminous coal, Greymouth, leaching.

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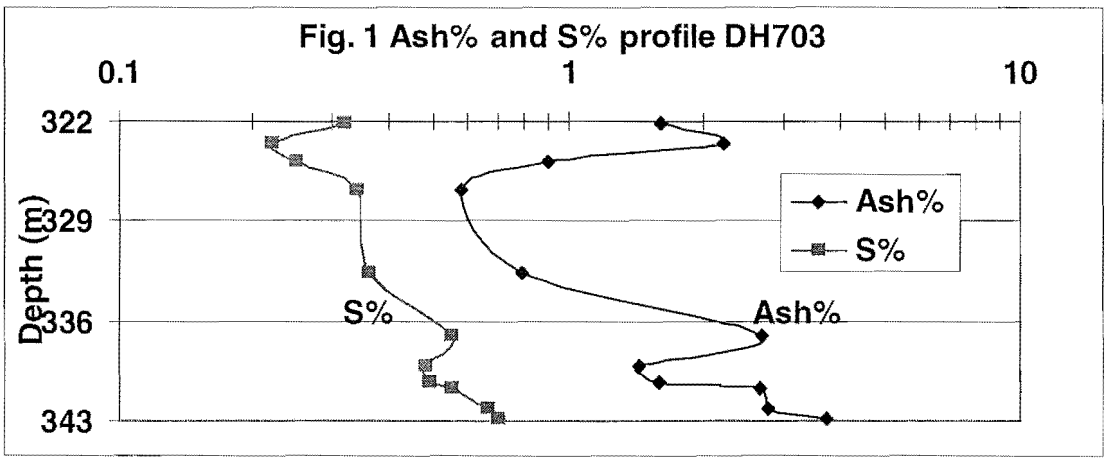

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Short communication

# Crocoite: an unusual mode of occurrence for lead in coal

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**Abstract**

What is believed to be a very unusual mode of occurrence for lead in coal has been identified as crocoite ($PbCrO_4$). As part of a larger study on trace elements and mineralogy in the Cretaceous Main Seam in New Zealand, crocoite was found in raw coal samples within the lower part of the coal seam. X-ray diffraction (XRD) and bulk chemical data from a SEM equipped with an energy dispersive X-ray analyser (EDXA) have confirmed the identity of this mineral. This is apparently the first time that crocoite has been reported in coal. Crocoite usually occurs only in the oxidised zone of lead mineral deposits. The occurrence of this mineral in the Main Seam coal implies that the deposit was exposed to an oxidising environment at some stage, most likely after coalification. Published by Elsevier Science B.V.

*Keywords:* crocoite; New Zealand; coal; mineralogy; geochemistry

## 1. Introduction

The geochemical variability of selected coal seams has been characterised as part of a larger study in the Greymouth coalfield of New Zealand. Two major economically important coal measures are present in the Greymouth coalfield: one is the Late Cretaceous bituminous Main Seam which is restricted to the Rewanui Coal Measures of the Paparoa Group; the other is the Tertiary bituminous Brunner Coal Measures. Fig. 1 shows the location of the Greymouth coalfield. In the study area, seven formations and members (from the Dunolie Formation at the top to the Jay Formation at the bottom) were recognised within the Paparoa Group (Fig. 2) (Newman and Newman, 1992; Ward, 1997). This paper focuses on the mode of occurrence of selected trace elements (Pb, Cr, and S) in the Main Seam. The mineralogy and geochemistry of major elements have been reported in an earlier study (Li et al., 1999). The Main Seam coal is high-volatile bituminous C (ASTM, 1991), with extremely low ash (typically 0.5–2%) and sulphur (typically $< 0.5\%$). The thickness of the coal seam varies (from 1 to 30 m), often abruptly (over tens of meters). The Main Seam is thought to have been deposited on floodplains associated with fluvial and lacustrine sequences (Bowman, 1982; Sherwood et al., 1992; Newman and Newman, 1992; Moore, 1996; Ward, 1997). The coal has generally low abundances of almost all trace elements on a whole coal basis, but high local concentrations of some elements (e.g., Pb, Cr). The unusual and hence

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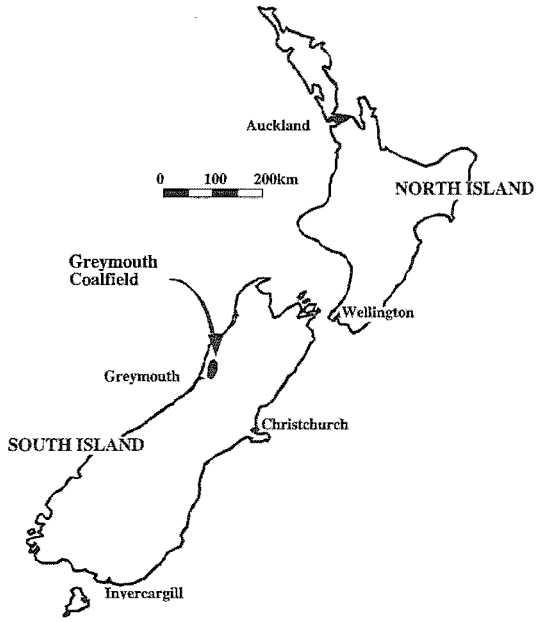


Fig. 1. The index map of New Zealand showing the location of the Greymouth Coalfield.

interesting occurrence of Pb is quite different from what appears in the literature on the modes of occurrence of Pb in other coals (see Swaine, 1990; Finkelman, 1980).

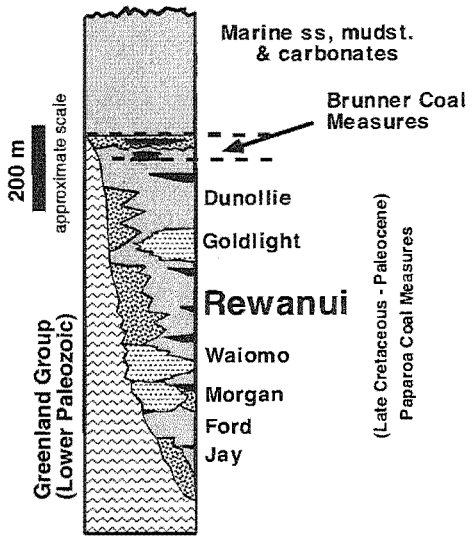


Fig. 2. The generalised stratigraphic sequence of Greymouth Coalfield. The Paparoa Group comprises a terrestrial sequence of alternating fluvial and lacustrine sandstone, mudstone, siltstone and coal, deposited in a rift basin.

## 2. Sampling and methods

About 60 samples of coal and rock were collected from two drillholes (703 and 755). All samples were reduced to $< 1$ mm. A subsplit of each sample was further reground to $< 60$ μm for trace element analysis by X-ray fluorescence spectrometry (XRF) and instrumental neutron activation analysis (INAA). The binocular microscope (magnification $\times 40$) has been used to examine the minerals present in low temperature ash (LTA) generated by an LFE LTA-302 machine. The LTA operating conditions were as follows: oxygen flow at 3 ml/min, RF power at $\sim 100$ W, and the temperature at the sample chambers is thought to be around 170°C. During microscopic observation of LTA, a bright orange–red mineral stood out. However, one of the major concerns was whether this unknown mineral was present in coal or was it an artifact of the LTA process. One possibility was that the unknown mineral was Fe oxide, perhaps as the oxidised product of pyrite or another Fe-bearing phase. To address this concern, polished blocks of raw coal samples were examined. Several examples of this mineral were found in two samples in the lower split of the Main Seam in drillhole 755. Interestingly, samples from a stratigraphically adjacent seam were also found to contain these types of crystals. Sizes of the crystals generally ranged from $< 0.1$ to 2 mm, adamantine to vitreous lustre, and were tabular in shape (Fig. 3); the coloration tended to be bright orange-to-red sometimes coated with a white, very thin film of another phase (possibly cerussite ($PbCO_3$)). The handpicked speci-

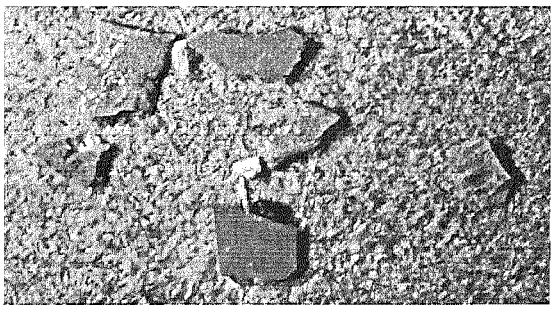

Fig. 3. The photograph of crocoite grains extracted from coal. The length of the longest grain is approximately 2 mm.

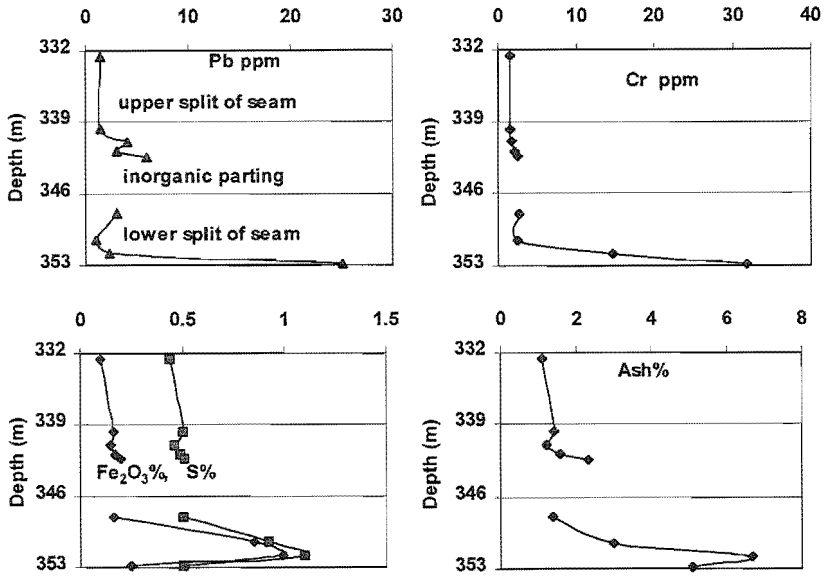


Fig. 4. Vertical profile of selected components (whole coal basis) in split Main Seam from core 755.

men grains of this mineral were then subjected to further elemental and mineralogical analysis.

## 3. Elemental chemistry

The selected elemental profiles of Pb, Cr, S, Fe and ash are given in Fig. 4. It was noted that the abundance of Pb and Cr increase dramatically at the lower part of the split. To identify the bright orange–red mineral, the elemental composition and the crystal structure data were needed. A few grains of this mineral were mounted and examined under SEM-EDXA to analyse the bulk elemental composition of this mineral. The semi-quantitative results of SEM-EDXA are given in Table 1. The analyses show that only Pb and Cr are present. After multiple analyses on six different grains, the semi-quantitative results consistently demonstrated that the unknown mineral is a Pb–Cr compound with molecular Pb/Cr ratio of approximately 1:1, and that it is probably an oxide.

Table 1
The SEM-EDXA analyses of the Cr–Pb mineral

| Analysis | | Pb | Cr | O[a] | Total |
|---|---|---|---|---|---|
| 1 | Wt.% | 37.12 | 8.04 | 9.89 | 55.05 |
| | Mol. Propn. | 0.188 | 0.162 | 0.649 | |
| 2 | Wt.% | 52.01 | 12.9 | 15.87 | 80.78 |
| | Mol. Propn. | 0.168 | 0.166 | 0.665 | |
| 3 | Wt.% | 53.52 | 14.97 | 18.41 | 86.90 |
| | Mol. Propn. | 0.152 | 0.170 | 0.678 | |
| 4 | Wt.% | 59.31 | 18.35 | 22.57 | 100.23 |
| | Mol. Propn. | 0.140 | 0.172 | 0.688 | |
| 5 | Wt.% | 62.13 | 15.16 | 18.65 | 95.94 |
| | Mol. Propn. | 0.171 | 0.166 | 0.663 | |
| 6 | Wt.% | 65.07 | 10.52 | 12.94 | 88.53 |
| | Mol. Propn. | 0.237 | 0.153 | 0.610 | |

Mol. Propn. = Molecular proportion.
[a]O% is calculated based on the Cr% in the formula of $PbCrO_4$.

## 4. X-ray diffraction results

The powder XRD study on the bulk LTA showed that the major minerals were clays (kaolinite, illite and mix-layered smectite) and quartz, with a small amount of sulphides (pyrite), carbonates (calcite, siderite, ankerite), and traces of sulphates (gypsum), salt (halite, sylvite) and other silicates (Li et al., 1999). For this study, an XRD pattern was obtained on a single crystal of the Pb–Cr mineral. The $d$ and intensity ($I/I1$) values of both this mineral and a JCPDS (Joint Committee on Powder Diffraction Standards) crocoite standard (Smith et al., 1967) are

Table 2
The single crystal X-ray diffraction pattern (sample data) and comparative standard crocoite diffraction pattern (crocoite data, taken from JCPDS# 8-209)

| Sample data | | Crocoite data | | Sample data | | Crocoite data | | Sample data | | Crocoite data | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $d$ (Å) | $I/I1$ | $d$ (Å) | $I/I1$ | $d$ (Å) | $I/I1$ | $d$ (Å) | $I/I1$ | $d$ (Å) | $I/I1$ | $d$ (Å) | $I/I1$ |
| 5.43 | 10 | 5.43 | 10 | 2.657 | 5 | 2.653 | 2 | 1.806 | 20 | 1.806 | 4 |
| 4.92 | 30 | 4.96 | 25 | 2.582 | 10 | 2.597 | 14 | 1.688 | 30 | 1.694 | 10 |
| 4.33 | 40 | 4.38 | 25 | 2.526 | 20 | 2.51 | 2 | 1.627 | 10 | 1.621 | 4 |
| 3.74 | 10 | 3.76 | 12 | 2.279 | 5 | 2.252 | 25 | 1.609 | 5 | 1.614 | 6 |
| 3.463 | 70 | 3.48 | 55 | 2.241 | 80 | 2.243 | 10 | 1.414 | 20 | 1.423 | 12 |
| 3.26 | 100 | 3.28 | 100 | 2.088 | 50 | 2.09 | 25 | 1.394 | 8 | 1.395 | 2 |
| 3.21 | 40 | 3.24 | 6 | 2.017 | 10 | 1.978 | 20 | 1.349 | 8 | 1.357 | 6 |
| 3.11 | 80 | 3.15 | 12 | 1.963 | 80 | 1.967 | 14 | 1.326 | 10 | 1.333 | 4 |
| 3 | 80 | 3.03 | 65 | 1.894 | 5 | 1.9 | 8 | 1.3 | 10 | 1.305 | 6 |
| 2.71 | 10 | 2.71 | 16 | 1.836 | 30 | 1.847 | 25 | 1.284 | 8 | 1.29 | 4 |

The $d$ values are quoted as angstrom unit (Å).

given in Table 2. The $d$ values are the perpendicular distance between different reflecting planes of crystal structure. Therefore, the $d$ value is the spacing of the planes that produce the given reflection. Both the $d$ values and intensities ($I/I1$) of the Pb–Cr mineral show very good agreement with those of the crocoite JCPDS data (Table 2). The difference between correspondent $d$ values of the sample data and standard data is well below the 2% experimental error that would normally be encountered (Smith et al., 1964). Therefore, the Pb–Cr mineral in the coal is confirmed as crocoite.

## 5. Geochemistry and discussion

Crocoite has not been reported as occurring in coal. Finkelman (1980) and Swaine (1990) all reported that PbS (galena) are the predominant mode of occurrence of Pb in coal. In vertical profiles of the Main Seam, Pb and Cr vary concomitantly (Fig. 4). Ash yield, Fe and S contents also vary together, but their variation is quite dissimilar from that of Pb and Cr. The high correlation between Pb and Cr (corr. coeff. $r = 0.89$) and lack of correlation between Pb and S ($r = -0.228$) is consistent with Pb occurring as crocoite. Furthermore, Pb and Cr do not correlate well with ash content ($r = 0.45$ and 0.65, respectively). This suggests that Pb and Cr are not directly derived from the same source as much of the other mineral matter. Moreover, the euhedral tabular with sharp angle morphology of crocoite grains (Fig. 3) suggests that they have not been transported far, if at all, and are not detrital in origin.

Crocoite ($PbCrO_4$) is known as a secondary mineral occurring in the oxidised zones of lead deposits (Gaines et al., 1997). There are no lead deposits that occur in the Greymouth coalfield. A speculation is that the numerous fault systems that occur within the coalfield may be the pathway of the source of lead. The exact mechanism can only be guessed at, but perhaps Pb has been secondarily leached from either basement or adjacent sedimentary rocks and then incorporated/fixed by organic matter and re-deposited within the coal. Under any emplacement mechanism, though, the presence of crocoite in the Main Seam coal represents an unusual and very interesting mineralogical occurrence.

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# Leaching of inorganics in the Cretaceous Greymouth coal beds, South Island, New Zealand

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**Abstract**

Leaching processes are believed to be responsible for the unusually low-ash content (sometimes less than 1%) of the thick (up to 35 m) Cretaceous coals located in the Greymouth coalfield, South Island, New Zealand. Although leaching of inorganics in peat is a generally accepted process, little is known about leaching after burial. The "Main" and "E" seams in the Greymouth coalfield show good correlation between low ash and bed thickness. The ash content, however, is often less than 1%, which is lower than most known modern analogues (i.e. peat). There are several lines of evidence that suggest that mineral matter may have been removed from the coal not only in the peat stage but also after burial. For example, etching features found in quartz grains and clay aggregates indicate that some leaching processes have taken place. In addition, liptinitic material (e.g., bitumen) in the cleat networks supports the conclusion that there has been some movement of solutions through the coal after burial. These solutions may have helped to remove some of the inorganics originally within the Greymouth coals. 

*Keywords:* Mineral matter; Inorganic; Cretaceous; Leaching; Post-burial; New Zealand

## 1. Introduction

The Late Cretaceous coal beds on the West Coast of the South Island in New Zealand are very important economically. These coals represent approximately 10% of New Zealand's total coal production and with the opening of new mines in the Greymouth coalfield (Fig. 1), this figure will double in the near future. Virtually all of New Zealand's bituminous coals occur in this region.

There are many coal beds present in the Greymouth coalfield (Gage, 1952; Nathan, 1978). This study focuses only on the Main and E coal beds of the Rewanui Coal Measures (Fig. 2). These two beds were deposited in fresh water environments associated with alternating sandstone, claystone, siltstone, mudstone, and other thinner and higher ash coal beds (Laird, 1972; Nathan, 1978; Newman and Newman, 1992; Ward, 1997). Both beds, especially the Main bed, have extremely low ash, with ranges of 0.58–2.5% (except for coal samples in contact with partings and floor rocks); these values are lower than those reported for most peat deposits (Shotyk et al., 1990; Neuzil et al., 1993).

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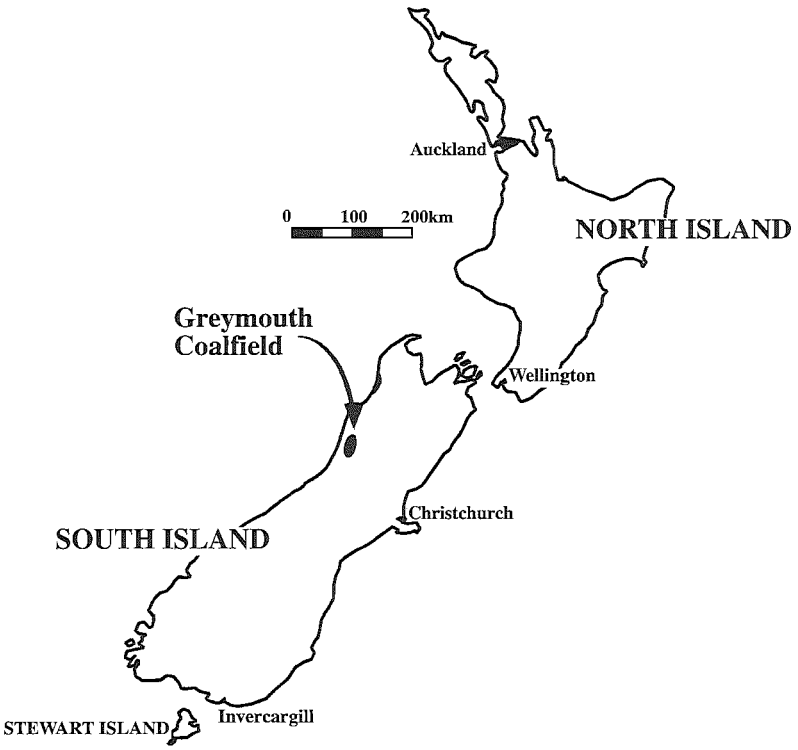


Fig. 1. Map of New Zealand showing the location of the Greymouth coalfield.

Most coal beds with ash yields less than 5% are interpreted to have been formed as raised bogs. Many researchers (Staub and Cohen, 1978; Cohen et al., 1987; Ruppert et al., 1993; Staub and Esterle, 1994; Cohen and Stack, 1996) have proposed that precipitation as the sole source of moisture, vegetation baffling, and flocculation of clays contribute to low concentration of inorganic matter in coal. These factors likely contribute to the formation of most low sulfur coals. However, the very low-ash yield (often below 2%) of the Greymouth coal seams puts them in a league of their own.

In order to preserve such anomalous ash yields in thick coal beds, two hypotheses could be proposed. First, that there was a very low concentration of inorganic matter during the peat stage. A quite unique depositional setting and processes would have been required to facilitate such low concentrations of inorganic materials. Indeed, even the peat-forming plants must have been unusually low in inorganics. In the second hypothesis, in addition to deposition in low-ash, raised peat-forming systems, inorganic matter was removed through leaching processes both during peat formation as well as after burial. The purpose of this paper is to discuss these two hypotheses and provide an explanation for the anomalously low-ash nature of the Greymouth coals.

## 2. Sampling and analysis

In order to understand the geological and geochemical factors that control coal quality and bed geometry in this region, two seams were investigated in detail. A total of 184 samples (89 from the E Seam and 95 from the Main Seam) were collected. These samples consisted of coal, inorganic partings as well as roof and floor sediments. The samples came from boreholes and underground and opencast mine sites.

Of the 184 samples collected, 141 were analysed for major elements using an X-ray Fluorescence

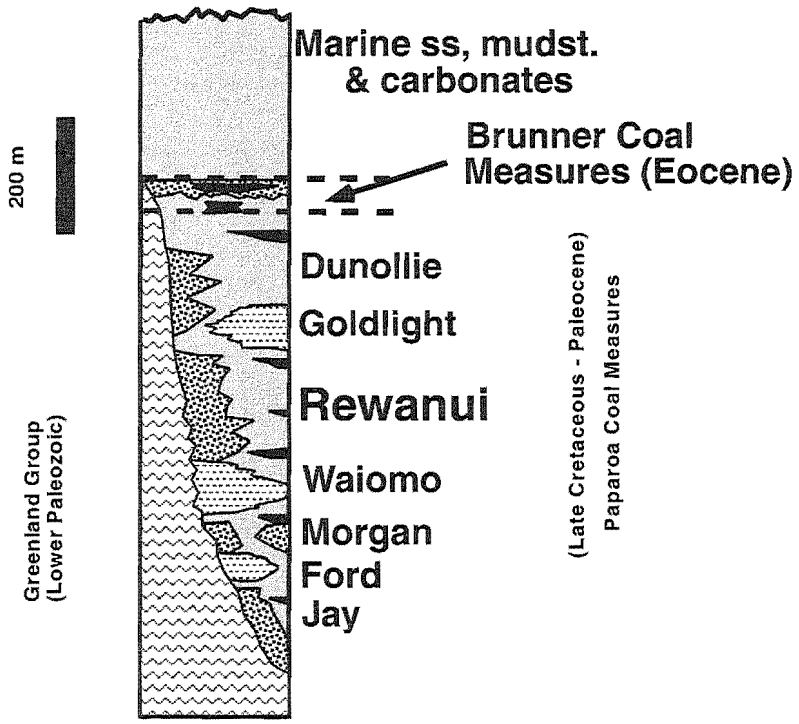


Fig. 2. Generalised stratigraphic sequences present in Greymouth coalfield, showing the Rewanui Coal Measures unconformably above basement rocks. The Tertiary–Cretaceous boundary lies about 20 m below the top of Rewanui Coal Measures. Not to scale.

Spectrometer (XRF). All 184 samples were also analysed for trace elements using XRF. Because the concentration of many trace elements falls below the detection limits of XRF, 73 out of 184 samples were also analysed using Instrumental Neutron Activation Analysis (INAA). However, this paper only focuses on the major elements rather than trace elements that were previously discussed by Li et al. (1999a). All sample locations and major element analyses are given in Table 1. X-ray diffraction (XRD) analysis was used to identify minerals present in low temperature ash (LTA) generated by an LFE LTA 302 machine. A scanning electron microscope equipped with an energy dispersive X-ray analyser (SEM-EDXA) was also employed to examine inorganics present in polished coal samples. In addition to these analyses, optical microscopy was also used to examine qualitative petrographic characteristics of select polished coal samples. Microscopic observations were carried out in both white and fluorescent mode. Sample preparation for petrography has been previously described by Li et al. (1999b, 2001).

## 3. Coal bed geometry

One of the most interesting features about the Greymouth coal beds is their great thickness. The coals, however, are laterally discontinuous both as a result of faulting and rapid facies changes. Drilling and coal resource exploration programs undertaken by government and private companies in the last 30 years have generated voluminous geological and coal quality data (unpublished reports and drilling logs).

In order to understand the relationship of bed geometry, spatial distribution of ash yield and sulphur content, we synthesized all the available quality data and combined these with the stratigraphic, geophysical and lithological data. Using these data, contour maps for thickness, ash yield and sulphur content have been constructed for both the Main and E Seams. The

Table 1
Sampling positions and major element analyses (on dry whole coal basis) for both Main and E seams

| Lab. No. | Field No. | Comment | Type[a] | Depth (m) | Ash (%) | $SiO_2$ (%) | $TiO_2$ (%) | $Al_2O_3$ (%) | $Fe_2O_3$ (%) | MnO (%) | MgO (%) | CaO (%) | $Na_2O$ (%) | $K_2O$ (%) | $P_2O_5$ (%) | $SO_3$ (%) | LOI (%) | S (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Main Seam at Rapahoe Sector* | | | | | | | | | | | | | | | | | | |
| 31195A | 703-RF1 | roof rocks | D/H | 319.9 | | 76.24 | 0.8 | 10.84 | 2.56 | 0.02 | 0.76 | 0.08 | <0.1 | 2.06 | 0.05 | 0.04 | 5.72 | 0.031 |
| 31196A | 703-RF2 | roof rocks | D/H | 321.1 | | 80.78 | 0.88 | 10.42 | 1.31 | 0.01 | 0.53 | 0.05 | <0.1 | 1.84 | 0.05 | <0.01 | 3.88 | 0.005 |
| 31197B | 703-RF3 | roof rocks | D/H | 321.8 | | 40.89 | 0.48 | 9.1 | 23.27 | 0.17 | 2.13 | 0.17 | <0.1 | 1.73 | 0.06 | 0.63 | 21.6 | 1.076 |
| 31247A | 703-A1 | coal | D/H | 322.2 | 1.60 | 1.652 | 0.033 | 0.397 | 0.027 | 0.023 | 0.009 | 0.036 | 0.047 | 0.009 | 0.001 | 0.047 | | 0.41 |
| 31249A | 703-B1 | coal | D/H | 323.5 | 2.20 | 1.833 | 0.030 | 0.190 | 0.030 | 0.022 | 0.007 | 0.030 | 0.038 | 0.004 | 0.001 | 0.039 | | 0.30 |
| 31251A | 703-C1 | coal | D/H | 324.9 | 0.90 | 0.559 | 0.012 | 0.195 | 0.027 | 0.000 | 0.005 | 0.024 | 0.029 | 0.003 | 0.000 | 0.017 | | 0.33 |
| 31254A | 703-D2 | coal | D/H | 326.8 | 0.58 | 0.300 | 0.007 | 0.152 | 0.026 | 0.000 | 0.005 | 0.021 | 0.022 | 0.002 | 0.000 | 0.013 | | 0.33 |
| 31259A | 703-F2 | coal | D/H | 332.6 | 0.79 | 0.284 | 0.008 | 0.173 | 0.195 | 0.000 | 0.006 | 0.029 | 0.009 | 0.002 | 0.000 | 0.04 | | 0.41 |
| 31261A | 703-G1 | coal | D/H | 337.2 | 2.68 | 1.795 | 0.030 | 0.355 | 0.377 | 0.027 | 0.005 | 0.026 | 0.028 | 0.004 | 0.001 | 0.012 | | 0.59 |
| 31264A | 703-H2 | coal | D/H | 339.2 | 1.43 | 0.571 | 0.010 | 0.384 | 0.310 | 0.014 | 0.005 | 0.025 | 0.024 | 0.004 | 0.001 | 0.047 | | 0.50 |
| 31266A | 703-I1 | coal | D/H | 340.3 | 1.59 | 1.123 | 0.032 | 0.247 | 0.115 | 0.016 | 0.003 | 0.014 | 0.026 | 0.003 | 0.001 | 0.005 | | 0.49 |
| 31268A | 703-J1 | coal | D/H | 340.8 | 2.65 | 1.618 | 0.029 | 0.682 | 0.202 | 0.027 | 0.006 | 0.026 | 0.025 | 0.006 | 0.001 | 0.038 | | 0.55 |
| 31272A | 703-K2 | coal | D/H | 342.1 | 2.76 | 1.561 | 0.089 | 0.513 | 0.399 | 0.028 | 0.006 | 0.070 | 0.030 | 0.007 | 0.002 | 0.027 | | 0.69 |
| 31274A | 703-L2 | coal | D/H | 342.9 | 3.74 | 2.025 | 0.053 | 1.121 | 0.373 | 0.037 | 0.016 | 0.023 | 0.028 | 0.049 | 0.003 | 0.016 | | 0.73 |
| 31198A | 703-FL1 | floor rocks | D/H | 343.1 | | 64.18 | 1.29 | 25.76 | 2.04 | <0.01 | 1.17 | 0.05 | 0.24 | 4.46 | 0.04 | <0.01 | 0.79 | 0.705 |
| 31199A | 703-FL2 | floor rocks | D/H | 343.4 | | 68.89 | 0.81 | 14.41 | 2.82 | 0.03 | 0.86 | 0.03 | 0.15 | 2.85 | 0.03 | 0.15 | 8.73 | 0.083 |
| 31200B | 703-FL3 | floor rocks | D/H | 343.6 | | 68.39 | 0.74 | 12.32 | 2.73 | 0.02 | 0.69 | 0.04 | 0.12 | 2.45 | 0.03 | 0.07 | 12.2 | 0.340 |
| 31192B | 755-RF1 | roof rocks | D/H | 330.21 | | 49.45 | 0.75 | 18.02 | 2.41 | 0.02 | 1.06 | 0.07 | 0.12 | 3.64 | 0.1 | 0.03 | 24.3 | 0.131 |
| 31193A | 755-RF2 | roof rocks | D/H | 330.94 | | 57.45 | 0.75 | 19.135 | 3.64 | 0.02 | 1.135 | 0.09 | 0.1 | 3.81 | 0.17 | 0.83 | 13.2 | 1.669 |
| 31194A | 755-RF3 | roof rocks | D/H | 331.53 | | 66.07 | 1.01 | 23.66 | 2.01 | 0.01 | 1.27 | 0.12 | 0.17 | 4.52 | 0.26 | <0.01 | 0.77 | 0.268 |
| 31229A | 755-A2 | coal | D/H | 332.55 | 1.10 | 0.692 | 0.013 | 0.101 | 0.080 | 0.000 | 0.007 | 0.067 | 0.030 | 0.004 | 0.001 | 0.052 | | 0.44 |
| 31232A | 755-B3 | coal | D/H | 339.7 | 1.41 | 0.823 | 0.017 | 0.279 | 0.151 | 0.000 | 0.006 | 0.025 | 0.030 | 0.004 | 0.001 | 0.036 | | 0.50 |
| 31236A | 755-D2 | coal | D/H | 341.92 | 1.58 | 0.916 | 0.019 | 0.368 | 0.158 | 0.000 | 0.006 | 0.028 | 0.022 | 0.004 | 0.001 | 0.023 | | 0.49 |
| *There is a parting present in drill hole 755 from 342.5 to 345.6 m (depth)* | | | | | | | | | | | | | | | | | | |
| 31225A | 755-N | dirty coal | D/H | 345.74 | | 27.898 | 0.355 | 5.421 | 3.100 | 0.022 | 1.390 | 2.966 | 0.048 | 1.165 | 0.013 | 0.416 | | 0.71 |
| 31226A | 755-O | dirty coal | D/H | 345.91 | | 34.575 | 0.400 | 4.227 | 0.519 | 0.412 | 0.247 | 0.037 | 0.066 | 0.993 | 0.012 | 0.004 | | 0.27 |
| 31239A | 755-P2 | coal | D/H | 348.00 | 1.39 | 0.798 | 0.025 | 0.284 | 0.152 | 0.000 | 0.007 | 0.027 | 0.023 | 0.004 | 0.001 | 0.035 | | 0.50 |
| 31242A | 755-Q2 | coal | D/H | 350.5 | 3.02 | 1.368 | 0.021 | 0.586 | 0.837 | 0.001 | 0.009 | 0.030 | 0.036 | 0.010 | 0.001 | 0.016 | | 0.92 |
| 31244A | 755-R2 | coal | D/H | 351.86 | 6.70 | 4.740 | 0.091 | 0.704 | 1.030 | 0.001 | 0.009 | 0.026 | 0.019 | 0.012 | 0.002 | 0.023 | | 1.10 |
| 31246A | 755-S | coal | D/H | 352.9 | 5.11 | 3.421 | 0.126 | 1.249 | 0.181 | 0.051 | 0.013 | 0.026 | 0.044 | 0.020 | 0.004 | 0.008 | | 0.50 |
| 31227A | 755-T | dirty coal | D/H | 353.25 | | 41.000 | 0.588 | 12.702 | 2.545 | 0.006 | 0.661 | 0.036 | 0.097 | 2.436 | 0.024 | 0.103 | | 0.78 |
| 31191A | 755-FL1 | floor rocks | D/H | 354.23 | | 77.77 | 0.76 | 12.29 | 1.59 | <0.01 | 0.87 | 0.05 | 0.05 | 2.64 | 0.02 | <0.01 | 3.62 | 0.005 |
| 31190A | 755-FL2 | floor rocks | D/H | 355.05 | | 72.25 | 0.81 | 15.03 | 1.94 | 0.01 | 1.04 | 0.04 | 0.15 | 3.13 | 0.03 | <0.01 | 5.59 | 0.018 |
| 31189A | 755-FL3 | floor rocks | D/H | 355.45 | | 63.14 | 0.87 | 18.04 | 2.08 | 0.01 | 1.16 | 0.04 | 0.17 | 3.83 | 0.11 | 0.06 | 9.81 | 0.033 |
| *E seam at Strongman Mine area* | | | | | | | | | | | | | | | | | | |
| 32135A | 283-A | coal | U/G | 0.025 | 5.11 | 3.142 | 0.1373 | 1.5667 | 0.048 | <0.01 | 0.036 | 0.01 | 0.007 | 0.118 | 0.022 | 5e−04 | 0.02 | 0.38 |
| 32136A | 283-B | coal | U/G | 0.25 | 3.53 | 1.355 | 0.0905 | 0.7342 | 0.9594 | 0.008 | 0.124 | 0.034 | 0.01 | 0.045 | 0.024 | 0.096 | 0.05 | 0.43 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 32137A | 283-C | coal | U/G | 0.75 | 2.76 | 0.458 | 0.0145 | 0.2675 | 1.65 | 0.017 | 0.166 | 0.027 | 0.005 | 0.015 | 0.007 | 0.1 | 0.03 | 0.40 |
| 32138A | 283-D | coal | U/G | 1.25 | 1.73 | 0.345 | 0.0071 | 0.1881 | 0.9406 | 0.008 | 0.114 | 0.022 | 0.006 | 0.012 | 0.005 | 0.056 | 0.03 | 0.35 |
| 32139A | 283-E | coal | U/G | 1.75 | 1.14 | 0.518 | 0.0117 | 0.246 | 0.2376 | 0.003 | 0.025 | 0.009 | 0.017 | 0.008 | 0.002 | 0.02 | 0.01 | 0.31 |
| 32140A | 283-F | coal | U/G | 2.25 | 1.22 | 0.485 | 0.01 | 0.2311 | 0.371 | 0.003 | 0.045 | 0.013 | 0.015 | 0.008 | 0.003 | 0.025 | 0.01 | 0.31 |
| 32141A | 283-G | coal | U/G | 2.75 | 1.05 | 0.493 | 0.0114 | 0.2017 | 0.1634 | 1e−03 | 0.023 | 0.057 | 0.019 | 0.009 | 0.002 | 0.057 | 0.01 | 0.31 |
| 32142A | 283-H | coal | U/G | 3.25 | 1.2 | 0.445 | 0.0087 | 0.2097 | 0.4234 | 0.003 | 0.056 | 0.017 | 0.004 | 0.004 | 0.001 | 0.021 | 0.01 | 0.28 |
| 32143A | 283-I | coal | U/G | 3.75 | 2.73 | 1.286 | 0.0134 | 0.1935 | 1.0305 | 0.01 | 0.08 | 0.029 | 0.007 | 0.004 | 0.002 | 0.057 | 0.02 | 0.30 |
| 32144A | 283-J | coal | U/G | 4.25 | 3.16 | 0.378 | 0.009 | 0.1797 | 2.2986 | 0.02 | 0.152 | 0.027 | 0.005 | 0.004 | 0.004 | 0.064 | 0.02 | 0.33 |
| 32145A | 283-K | coal | U/G | 4.75 | 4.29 | 0.305 | 0.0095 | 0.1803 | 3.2956 | 0.025 | 0.263 | 0.033 | 0.005 | 0.003 | 0.006 | 0.113 | 0.06 | 0.38 |
| 32146A | 283-L | coal | U/G | 5.15 | 4.58 | 0.364 | 0.0065 | 0.3454 | 3.2239 | 0.022 | 0.338 | 0.043 | 0.005 | 0.003 | 0.007 | 0.165 | 0.06 | 0.39 |
| 32147A | 283-M | coal with partings | U/G | 5.35 | 24.03 | 13.54 | 0.3257 | 6.0072 | 0.3426 | <0.01 | 0.331 | 1.021 | 0.039 | 1.416 | 0.796 | 0.031 | 0.15 | 0.22 |
| 32083A | 637-RF1 | roof rocks | U/G | | | 67.82 | 0.91 | 22.26 | 1.88 | 0.01 | 1.24 | 0.22 | 0.11 | 4.05 | 0.22 | 0.12 | 1.45 | |
| 32084A | 637-RF2 | roof rocks | U/G | | | 61.43 | 1.12 | 26.93 | 2.24 | 0.01 | 1.44 | 0.24 | <0.1 | 5.03 | 0.25 | 0.19 | 1.1 | |
| 32085A | 637-Top | coal | U/G | 0.25 | 2.8 | 1.237 | 0.0243 | 0.7289 | 0.5352 | 0.005 | 0.078 | 0.019 | 0.012 | 0.051 | 0.013 | 0.06 | 0.04 | 0.42 |
| 32086A | 637-B | coal | U/G | 0.75 | 2.04 | 0.277 | 0.0056 | 0.164 | 1.1161 | 0.007 | 0.277 | 0.052 | 0.005 | 0.002 | 0.001 | 0.119 | 0.02 | 0.34 |
| 32087A | 637-C | coal | U/G | 1.25 | 0.92 | 0.411 | 0.0076 | 0.1839 | 0.1854 | 6e−04 | 0.049 | 0.022 | 0.014 | 0.005 | 0.001 | 0.032 | 0.01 | 0.28 |
| 32088A | 637-D | coal | U/G | 1.75 | 1.65 | 1.134 | 0.0169 | 0.2969 | 0.1069 | 3e−04 | 0.026 | 0.014 | 0.02 | 0.003 | 8e−04 | 0.022 | 0.01 | 0.23 |
| 32089A | 637-E | coal | U/G | 2.25 | 1.81 | 1.175 | 0.0209 | 0.35 | 0.1548 | 2e−04 | 0.04 | 0.016 | 0.017 | 0.005 | 0.001 | 0.02 | 0.01 | 0.21 |
| 32090A | 637-F | coal | U/G | 2.75 | 1.15 | 0.651 | 0.0104 | 0.216 | 0.1821 | 0.001 | 0.035 | 0.012 | 0.011 | 0.002 | 6e−04 | 0.019 | 0.01 | 0.21 |
| 32091A | 637-Mid | coal | U/G | 3.25 | 1.01 | 0.407 | 0.0071 | 0.167 | 0.3065 | 0.002 | 0.058 | 0.017 | 0.005 | 0.002 | 7e−04 | 0.029 | 0.01 | 0.22 |
| 32092A | 637-G | coal | U/G | 3.75 | 1.51 | 0.532 | 0.0085 | 0.2406 | 0.4893 | 9e−04 | 0.121 | 0.036 | 0.011 | 0.005 | 9e−04 | 0.053 | 0.01 | 0.20 |
| 32093A | 637-H | coal | U/G | 4.25 | 0.92 | 0.585 | 0.009 | 0.2209 | 0.0503 | 2e−04 | 0.01 | 0.009 | 0.018 | 0.003 | 7e−04 | 0.009 | 0.01 | 0.21 |
| 32094A | 637-I | coal | U/G | 4.75 | 0.88 | 0.421 | 0.0076 | 0.1736 | 0.1347 | 1e−03 | 0.033 | 0.034 | 0.014 | 0.005 | 0.001 | 0.042 | 0.01 | 0.23 |
| 32095A | 637-J | coal | U/G | 5.25 | 5.15 | 0.318 | 0.0073 | 0.1855 | 1.9005 | 0.016 | 0.794 | 1.083 | 0.007 | 0.005 | 0.004 | 0.358 | 0.47 | 0.28 |
| 32097A | 637-L | coal | U/G | 6.25 | 2.75 | 0.738 | 0.0157 | 0.317 | 1.4315 | 0.013 | 0.087 | 0.023 | 0.008 | 0.008 | 0.003 | 0.073 | 0.03 | 0.26 |
| 32098A | 637-M | coal contact floor | U/G | 6.75 | 15.98 | 10.65 | 0.1734 | 3.5862 | 0.2119 | <0.01 | 0.159 | 0.199 | 0.016 | 0.7 | 0.204 | 0.006 | 0.11 | 0.21 |
| 32099A | 637-FL1 | floor rocks | U/G | | | 61.09 | 1.14 | 26.82 | 1.52 | <0.01 | 1.42 | 0.4 | <0.1 | 6.43 | 0.44 | <0.01 | 0.42 | |
| 32100A | 637-FL2 | floor rocks | U/G | | | 70.72 | 0.99 | 20.11 | 1.8 | 0.01 | 1.12 | 0.14 | <0.1 | 4.18 | 0.27 | <0.01 | 0.99 | |
| 31638A | P532-RF | roof rocks | U/G | | | 60.21 | 0.7586 | 20.921 | 2.5044 | 0.009 | 1.572 | 0.274 | 0.119 | 4.25 | 0.274 | <0.01 | 0.74 | |
| 31640A | P532A-B | coal | U/G | 0.1 | 1.63 | 0.77 | 0.0134 | 0.4898 | 0.2248 | 0.002 | 0.023 | 0.022 | 0.005 | 0.014 | 0.005 | 0.017 | 0.01 | 0.41 |
| 31641A | P532A-C | coal | U/G | 1.6 | 1.3 | 0.798 | 0.0365 | 0.3649 | 0.0477 | 4e−04 | 0.007 | 0.006 | 0.008 | 0.006 | 8e−04 | 0.002 | 0.61 | 0.30 |
| 31642A | P532A-D | coal | U/G | 3.64 | 4.72 | 2.575 | 0.0415 | 1.1795 | 0.396 | 0.002 | 0.041 | 0.094 | 0.012 | 0.1 | 0.181 | 0.011 | 0.55 | 0.27 |
| 31643A | P532A-E | chuckies | U/G | | | 87.98 | 0.56 | 5.36 | 0.34 | <0.01 | 0.29 | 1.25 | <0.1 | 1.63 | 0.96 | <0.01 | 1.9 | |
| 31647A | P532-Pt | partings | U/G | 4.04 | | 49.61 | 0.5959 | 18.221 | 1.8412 | 0.008 | 1.192 | 0.306 | 0.084 | 3.476 | 0.52 | <0.01 | 0.93 | |
| 31645A | P532B | coal with parting | U/G | 4.7 | 12.7 | 7.557 | 0.1168 | 3.1883 | 0.2064 | 0.006 | 0.119 | 0.416 | 0.021 | 0.479 | 0.378 | 0.008 | 1.63 | 0.28 |
| 31646A | P532-FL | floor rocks | U/G | | | 41.63 | 0.6384 | 19.456 | 7.0452 | 0.046 | 1.801 | 0.175 | <0.1 | 3.374 | 0.274 | 0.122 | 2.05 | |
| 31631A | 99-2A-RF | roof rocks | U/G | | | 66.01 | 0.6962 | 16.012 | 1.8686 | 0.009 | 0.925 | 1.493 | 0.092 | 2.84 | 1.118 | <0.01 | 0.46 | |
| 31632A | 99-2A-B | coal | U/G | 3 | 0.6 | 0.282 | 0.0062 | 0.1138 | 0.0987 | 2e−04 | 0.02 | 0.011 | 0.017 | 0.002 | 6e−04 | 0.022 | 0.74 | 0.28 |
| 31634A | 99-2B-B | coal | U/G | 4 | 0.57 | 0.277 | 0.0046 | 0.1355 | 0.0848 | 3e−04 | 0.014 | 0.009 | 0.01 | 7e−04 | 3e−04 | 0.01 | 0.37 | 0.24 |
| 31635A | 99-2B-C | coal | U/G | 5 | 2.52 | 0.155 | 0.0045 | 0.1565 | 1.917 | 0.017 | 0.1 | 0.02 | 0.014 | 0.002 | 0.003 | 0.062 | 2.49 | |

*(continued on next page)*

Table 1 (*continued*)

| Lab. No. | Field No. | Comment | Type[a] | Depth (m) | Ash (%) | $SiO_2$ (%) | $TiO_2$ (%) | $Al_2O_3$ (%) | $Fe_2O_3$ (%) | MnO (%) | MgO (%) | CaO (%) | $Na_2O$ (%) | $K_2O$ (%) | $P_2O_5$ (%) | $SO_3$ (%) | LOI (%) | S (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *E seam at Strongman Mine area* | | | | | | | | | | | | | | | | | | |
| 32103A | OPC-Top | coal | O/C | 0.6 | 2.55 | 1.681 | 0.026 | 0.5836 | 0.162 | 0 | 0.013 | 0.004 | 0.021 | 0.042 | 0.001 | 0.003 | 0.01 | 0.43 |
| 32104A | OPC-A | coal | O/C | 1.2 | 1.19 | 0.751 | 0.0114 | 0.358 | 0.0265 | 0 | 0.005 | 0.003 | 0.017 | 0.01 | 7e − 04 | 0.002 | 0 | 0.36 |
| 32105A | OPC-B | coal | O/C | 1.8 | 1.49 | 1.05 | 0.018 | 0.3579 | 0.02 | 0 | 0.004 | 0.004 | 0.019 | 0.008 | 8e − 04 | 0.003 | 0.01 | 0.31 |
| 32106A | OPC-C | coal | O/C | 2.4 | 1.04 | 0.659 | 0.0102 | 0.254 | 0.0585 | 2e − 04 | 0.011 | 0.005 | 0.019 | 0.008 | 5e − 04 | 0.008 | 0.01 | 0.29 |
| 32107A | OPC-D | coal | O/C | 3 | 1.35 | 0.917 | 0.0154 | 0.3353 | 0.0292 | 0 | 0.004 | 0.003 | 0.02 | 0.01 | 7e − 04 | 0.005 | 0.01 | 0.27 |
| 32354A | OPC-E | coal | O/C | 3.6 | 0.83 | 0.492 | 0.0082 | 0.2485 | 0.0248 | 0 | 0.003 | 0.003 | 0.02 | 0.005 | 4e − 04 | 0.016 | 0.01 | 0.32 |
| 32108A | OPC-F | coal | O/C | 4.2 | 1.69 | 1.052 | 0.0206 | 0.4633 | 0.0474 | 0 | 0.013 | 0.009 | 0.018 | 0.037 | 0.011 | 0.004 | 0.02 | 0.24 |
| 32109A | OPC-G | coal | O/C | 4.8 | 2.26 | 1.108 | 0.0217 | 0.5584 | 0.3302 | 0.003 | 0.067 | 0.028 | 0.018 | 0.064 | 0.029 | 0.026 | 0.01 | 0.26 |
| 32110A | OPC-H | coal | O/C | 5.4 | 1.07 | 0.575 | 0.0125 | 0.2585 | 0.1266 | 6e − 04 | 0.019 | 0.008 | 0.024 | 0.015 | 0.002 | 0.015 | 0.01 | 0.27 |
| 32111A | OPC-I | coal | O/C | 6 | 1.25 | 0.557 | 0.011 | 0.3077 | 0.2467 | 0.001 | 0.045 | 0.013 | 0.02 | 0.013 | 0.005 | 0.02 | 0.01 | 0.29 |
| 32112A | OPC-J | coal | O/C | 6.6 | 10.12 | 4.891 | 0.1226 | 3.2092 | 0.1614 | 0 | 0.119 | 0.479 | 0.018 | 0.507 | 0.518 | 0.017 | 0.08 | 0.24 |
| 32113A | OPC-K | coal with partings | O/C | 6.7 | 13.25 | 6.948 | 0.1584 | 3.8935 | 0.2156 | 0 | 0.166 | 0.552 | 0.021 | 0.723 | 0.49 | 0.009 | 0.07 | 0.23 |
| 32114A | OPC-L | partings | O/C | 6.8 | | 33.62 | 0.6796 | 17.149 | 5.5386 | 0.038 | 1.512 | 0.318 | 0.03 | 3.811 | 0.254 | 0.165 | 0.46 | 0.13 |
| 32115A | OPC-M | coal | O/C | 6.96 | 5.86 | 2.363 | 0.0267 | 2.1702 | 0.0439 | 0 | 0.02 | 0.494 | 0.025 | 0.049 | 0.608 | 0.015 | 0.04 | 0.29 |
| 32116A | OPC-N | coal with partings | O/C | 7.46 | 16.23 | 9.22 | 0.1773 | 4.2901 | 0.314 | 0 | 0.211 | 0.53 | 0.029 | 0.896 | 0.438 | 0.02 | 0.11 | 0.25 |
| 32119A | OPC-FL | floor rocks | O/C | | | 60.33 | 1.08 | 27.42 | 2.12 | 0.01 | 1.38 | 0.13 | 0.12 | 5.98 | 0.3 | 0.09 | 1.12 | |
| 32120A | O/C2-RF | roof rocks | O/C | | | 73.03 | 0.83 | 13.26 | 7.44 | 0.05 | 2.08 | 0.19 | <0.1 | 2.6 | 0.07 | 0.10 | 0.56 | |
| 32121A | O/C2-A | coal | O/C | 0.15 | 3.09 | 2.408 | 0.0297 | 0.4806 | 0.0384 | 0 | 0.023 | 0.003 | 0.005 | 0.094 | 0.005 | 9e − 04 | 0.01 | 0.29 |
| 32122A | O/C2-Pt | partings | O/C | 0.21 | | 61.67 | 0.5476 | 19.581 | 1.7841 | 0.009 | 0.98 | 0.141 | 0.097 | 3.1 | 0.168 | 0.009 | 0.63 | 0.02 |
| 32124A | O/C2-B | coal | O/C | 1.03 | 3.08 | 2.176 | 0.0373 | 0.6889 | 0.0768 | 6e − 04 | 0.019 | 0.014 | 0.015 | 0.043 | 0.01 | 0.005 | 0.01 | 0.30 |
| 32125A | O/C2-C | coal | O/C | 1.8 | 1.68 | 0.707 | 0.0119 | 0.3809 | 0.4649 | 0.004 | 0.058 | 0.016 | 0.01 | 0.009 | 0.002 | 0.024 | 0.01 | 0.27 |
| 32126A | O/C2-D | coal | O/C | 2.6 | 3.18 | 2.31 | 0.0402 | 0.6651 | 0.0556 | 0 | 0.014 | 0.016 | 0.022 | 0.026 | 0.017 | 0.005 | 0.01 | 0.23 |
| 32127A | O/C2-E | coal | O/C | 3.4 | 4.1 | 2.503 | 0.0403 | 0.7367 | 0.385 | 8e − 04 | 0.09 | 0.146 | 0.016 | 0.022 | 0.11 | 0.032 | 0.02 | 0.23 |
| 32128A | O/C2-F | coal | O/C | 4.2 | 1.57 | 0.795 | 0.0161 | 0.4012 | 0.236 | 3e − 04 | 0.051 | 0.013 | 0.014 | 0.009 | 9e − 04 | 0.018 | 0.01 | 0.27 |
| 32129A | O/C2-G | coal | O/C | 5 | 1.83 | 0.708 | 0.0164 | 0.3138 | 0.6283 | 0.006 | 0.043 | 0.016 | 0.018 | 0.011 | 0.002 | 0.05 | 0.02 | 0.29 |
| 32130A | O/C2-H | coal | O/C | 5.8 | 3.42 | 1.581 | 0.0479 | 0.9085 | 0.3035 | 0.003 | 0.027 | 0.19 | 0.011 | 0.058 | 0.228 | 0.033 | 0.03 | 0.28 |
| 32131A | O/C2-FL | floor rocks | O/C | | | 62.92 | 0.98 | 25.7 | 1.84 | <0.01 | 1.35 | 0.23 | 0.1 | 5.56 | 0.49 | 0.04 | 0.93 | |
| 32117A | Fault-Top | coal | O/C | 0.8 | 2.07 | 1.325 | 0.0311 | 0.6165 | 0.0372 | 0 | 0.012 | 0.006 | 0.013 | 0.031 | 0.003 | 0.004 | 0.02 | 0.46 |
| 32118A | Fault-Mid | coal | O/C | 1.6 | 2.8 | 1.898 | 0.0317 | 0.6653 | 0.0918 | 6e − 04 | 0.021 | 0.006 | 0.015 | 0.05 | 0.003 | 0.004 | 0.02 | 0.35 |

(a) All coal sample data are reported in percentages on a whole coal dry basis, whereas roof and floor rocks, chuckies, and partings are on a dry basis. All coal samples are ply samples except where stated otherwise.

(b) Sampling depth data for E seam at Strongman area are measured in the underground mine from the roof rocks downwards (i.e. not true depth from the surface), whereas data for Main seam are true depth from the surface.

[a] Key to Type: D/H = sampled from drill hole core; U/G = sampled from underground mine; O/C = sampled from open cast mine sites.

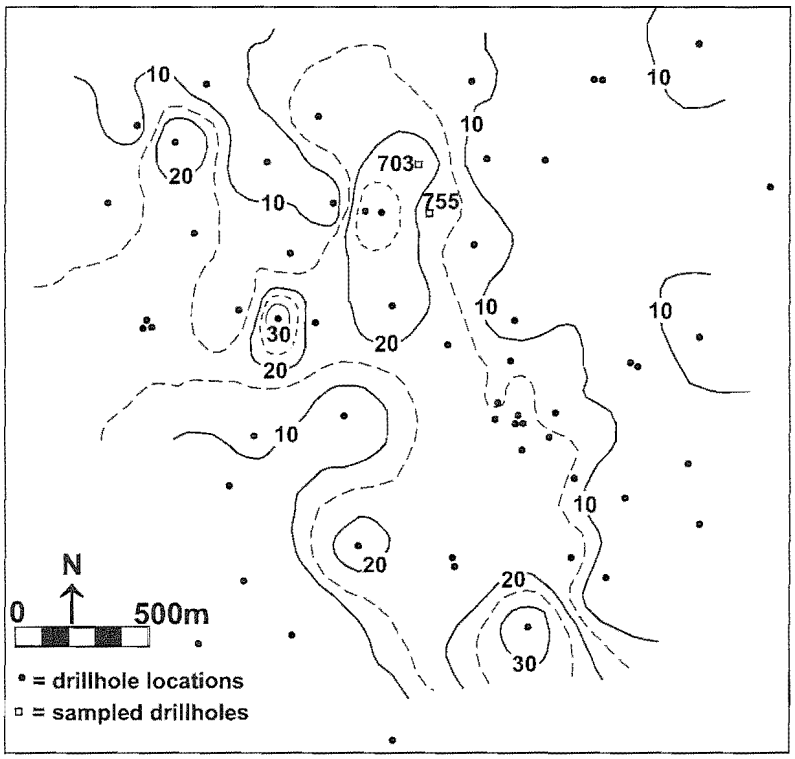


Fig. 3. Thickness (m) map of Main Bed at Rapahoe, Greymouth coalfield, based on 63 drillholes.

thickness for the two seams and the ash variability in the Main Seam is shown in Figs. 3–5. The thickness of Main Seam ranges from 1 to 35 m (typically 10 to 20 m) (Fig. 3). The thickest part of the Main bed trends approximately north–south, and it thins both to the east and west. Thickness decreases are a result of splitting (Moore, 1996b).

The E bed, which is stratigraphically higher (for approximately 20–50 m), shows a slightly different geometry (Fig. 4). The thickest part (up to 14 m) of the E bed is present only in the northern part of the basin. Towards the south in the basin, where the Main bed is located, the E bed is usually less than 4-m thick.

## 4. Inorganic geochemistry

### *4.1. Low-ash nature*

What makes the Cretaceous Greymouth coal beds anomalous is their extremely low ash yields. For example, the two beds studied generally have ash yields of 1% to 3% (Table 1). Most coal ply samples have ash yields in the range of 0.58–2.5% (air dry basis—adb) except for a few dirty coal samples associated with partings or in close proximity to floor or roof rocks. These higher ash intervals sometimes approach ash yields of 24% or higher. Other Cretaceous coals worldwide have ash yields (dry whole bed basis) ranging from 10% to 25% (McCabe and Parrish, 1992). In fact, most coals, irrespective of age, have ash yields ranging from 5% to 10%, and rarely below 5%. It is also notable that even low ash peat has ash yields generally in the range of 1–5% (Ruppert et al., 1993; Moore et al., 1999) (Table 2).

Fig. 5 illustrates that the lowest ash yields for the Main Seam are coincident with the thickest part of the bed (compared with Fig. 3). Towards all margins, ash yields tend to increase, especially towards the east and northwest margins. The two highest ash zones are located in the northwest and eastern parts

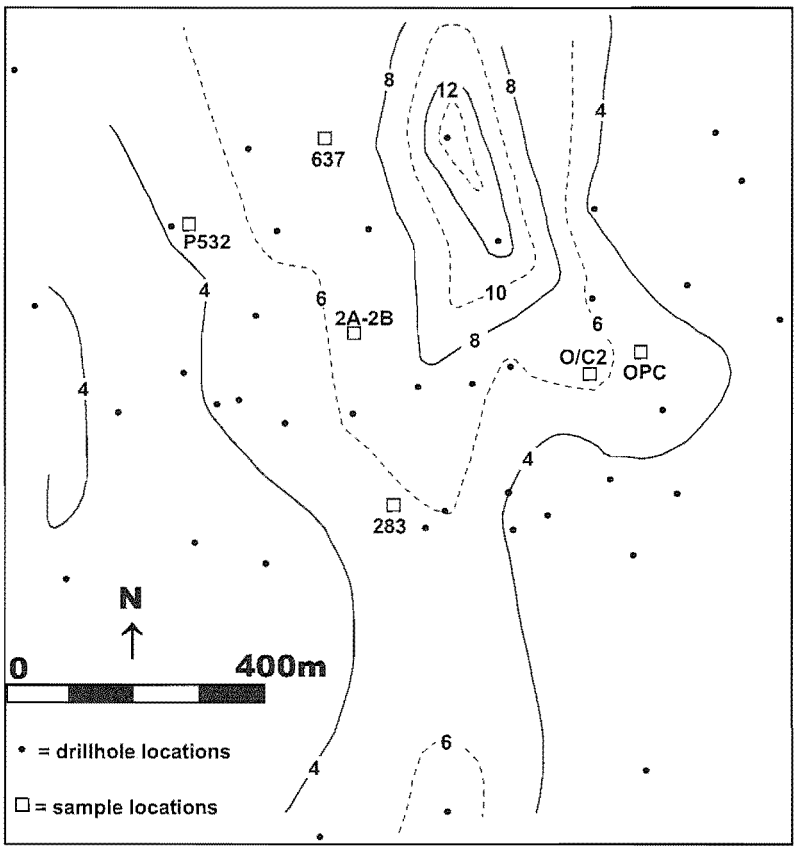


Fig. 4. Thickness (m) map of E Bed at Strongman Mine, based on unpublished drillhole log data and many hundreds of underground measurements.

of the study area. Bowman (1982) envisages that the northwestern part of the study area was locally of higher relief and thus provided a ready source of sediment. The higher ash areas in the east are probably related to a palaeochannel, which periodically flooded the peat margins (Bowman, 1982; Newman and Newman, 1992).

In order to further understand ash yield, six vertical bed profiles for the E Seam and five vertical profiles for the Main Seam were investigated in detail. Fig. 6 gives an ash profile of the Main Seam in drill hole 703. Although ash yields are around 2% or higher (adb) at both the top and the bottom of the bed, the ash yield decreases dramatically toward the centre where it is as low as 0.58%. All other bed profiles investigated followed a similar distribution pattern.

### *4.2. Ash mineralogy*

Ash mineralogy was also investigated in both the Main and E Seams. Ash consists mostly of clays (mainly kaolinite and illite with minor amounts of smectite) and quartz in both beds. Minor amounts of pyrite were also common and the Main Seam contained little or no carbonate. In contrast, the E bed commonly contained carbonates (siderite, calcite, ankerite) and phosphates (apatite, crandallite, etc.) but with no, or trace, sulphides (pyrite). Both beds have trace amounts of sulphates, oxides, salts, and

Table 2
The ash yield range of Greymouth coals compared with modern peats and other Cretaceous coals (air dry basis)

| | Ash (%) range | Average ash (%) | No. of samples | Source |
|---|---|---|---|---|
| *Deposit* | | | | |
| Three Indonesian peats average | | | | |
| Top peat | 0.40–4.66 | 1.52 | 32 | Neuzil et al. (1993) and Ruppert et al. (1993) |
| Middle peat | 0.13–3.66 | 1.07 | 63 | Neuzil et al. (1993) and Ruppert et al. (1993) |
| Bottom peat | 5.21–19.87 | 11.79 | 13 | Neuzil et al. (1993) and Ruppert et al. (1993) |
| 35 Canadian peats | 4.8–37.4 | 9.5 | 158 | Shotyk et al., 1992 |
| New Zealand peat | 1.6–10 | 5.4 | 25 | Shearer (personal communication, 2001) and Moore et al. (1999) |
| *Cretaceous coals in this study* | | | | |
| Main Seam coal | 0.5–12.4 | 4.73 | 60 drill holes | This study |
| E Seam coal | 0.83–15.98 | 2.87 | 46 | This study |
| *Other Cretaceous coals* | | | | |
| Five Australian coals | 4.4–23.3 | 10.7 | 15 | Fielding (1992) |
| Canadian coals | 4–30 | 14 | 291 | Langenberg et al. (1992) |
| New Mexican coal | 15.8–29.6 | 20.9 | 29 | Hoffman et al. (1992) |

other silicates (Li et al., 1999b). The presence of crocoite was also noted by Li et al. (2001) in both beds. As with other coal beds, it was observed that the grain size of inorganics increased as ash yields became elevated. This is especially true for quartz and clay aggregates, which compose the bulk of the

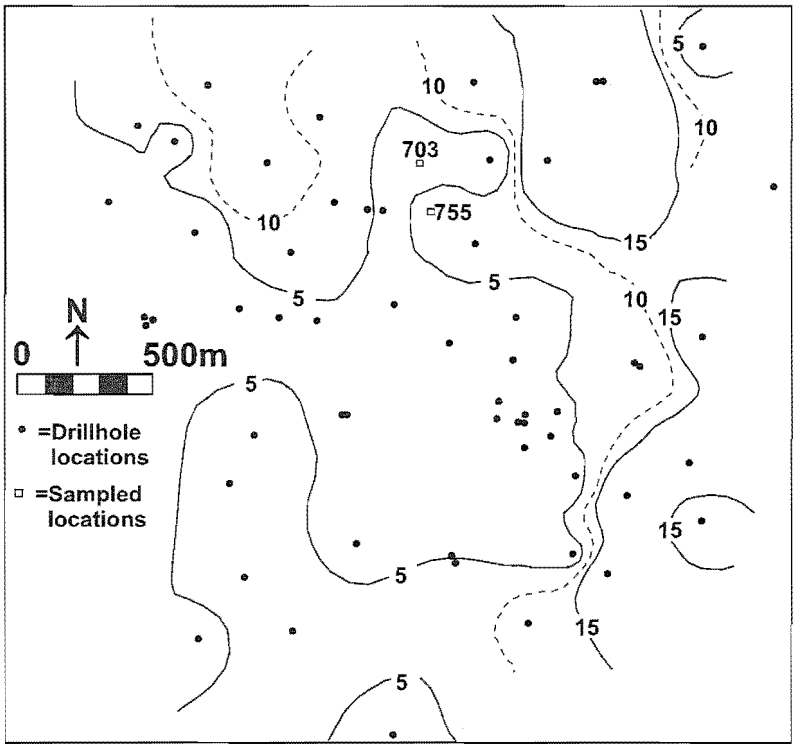


Fig. 5. Ash yield (%) isopachs of Main Bed at Rapahoe, Greymouth coalfield, based on 63 drillholes.

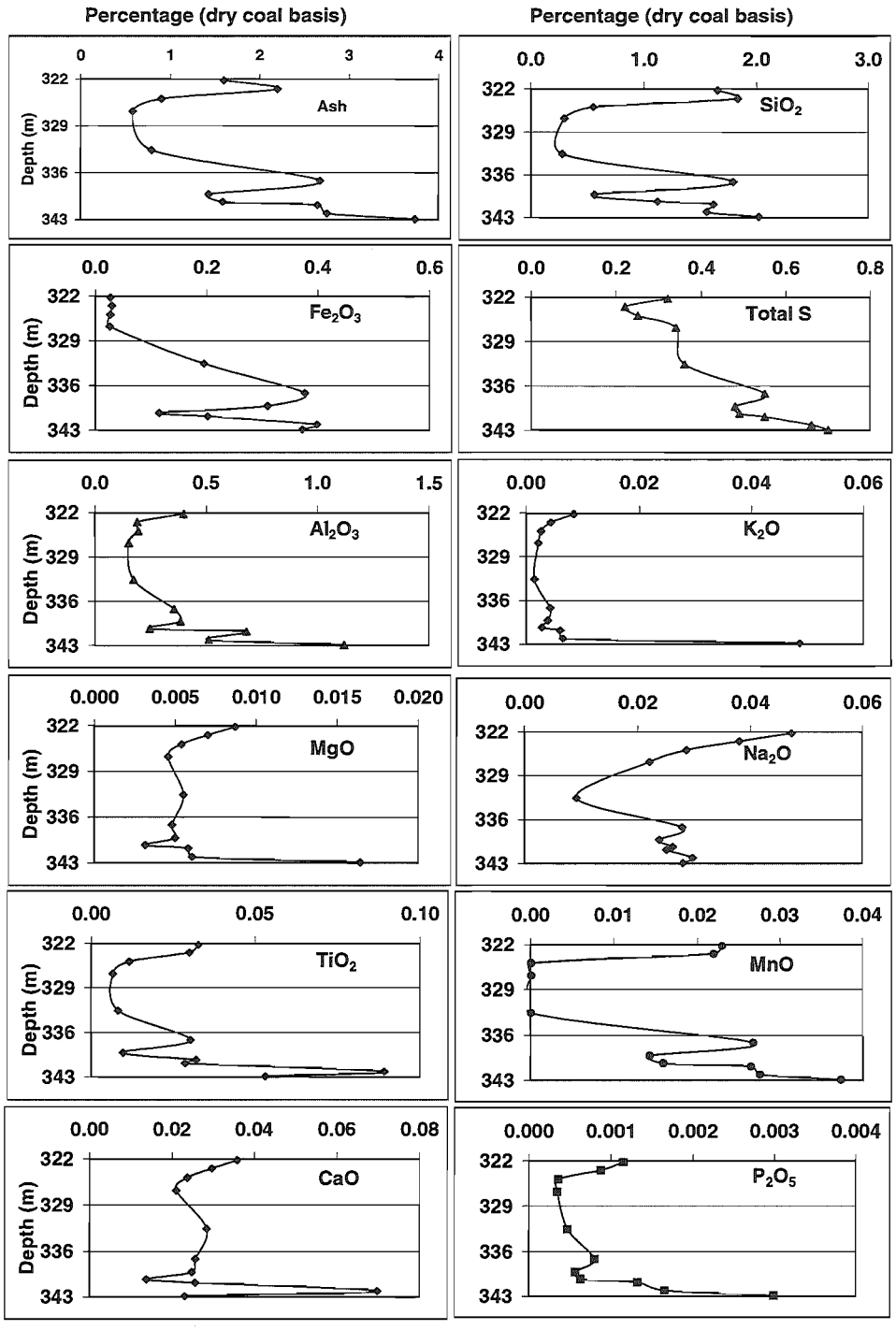


Fig. 6. Profiles of ash and major elements for the Main bed in drill hole 703.

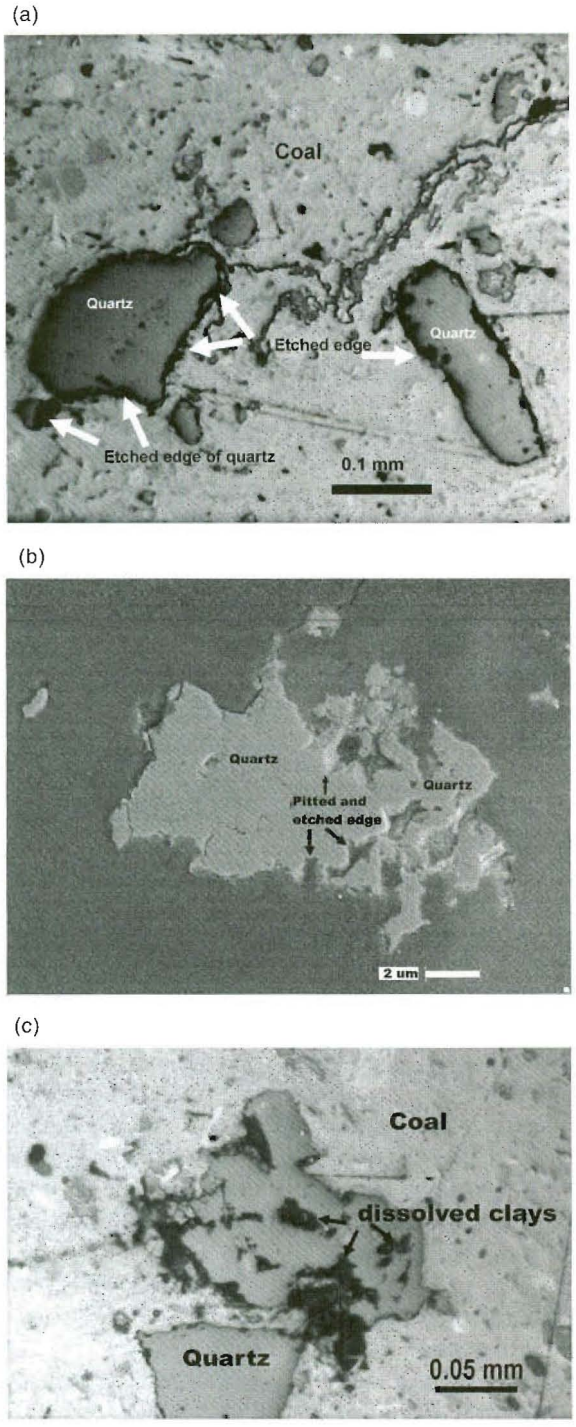


Fig. 7. Photomicrographs show some leached features of quartz and clay minerals in Main bed. (a) Etched edge of quartz grains suggests that the quartz was dissolved during the peat stage and after burial. Reflected light. (b) Backscattered electron photomicrograph of micron-sized quartz grain showing dissolved boundaries and etching characteristics. (c) Clay minerals (mainly kaolinite) have been dissolved leaving open holes and/or pores. Reflected light.

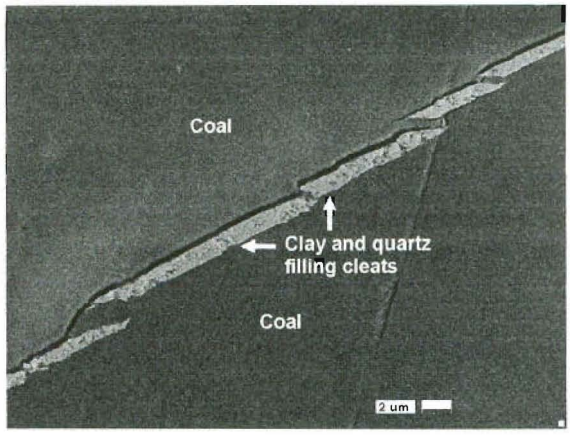


Fig. 8. SEM photomicrograph of cleat-filling clay minerals and quartz indicate secondary movement of mineral matter after burial in Main bed.

ash. Another observation is that some quartz grains show clear dissolution along boundaries (Fig. 7a–c). Dissolution of quartz was also observed in peats by Cohen (1972) and Andrejko et al. (1983). Clay minerals also show leaching features, such as dissolved boundaries, and sometimes the aggregates have been almost totally leached, being represented only by tiny residues. Finally, quartz, clays and carbonates (mainly calcite) are often distributed along cleats in the Greymouth coals (Fig. 8), suggesting post-burial mobilization of these minerals.

### 4.3. Geochemistry

A profile of major elements observed in DH 703 is shown in Fig. 6. $SiO_2$ follows the same vertical variation trend as ash yield, suggesting that $SiO_2$ is the primary controlling factor for ash yield, although $Al_2O_3$ (from clays) also makes a significant contribution. $Fe_2O_3$ and S show a similar trend across the whole profile and this trend is very different to that of the total ash yield and $SiO_2$. Based on the vertical

variations in the seams, the major components could be classified into two groups. Group I includes $SiO_2$, $Al_2O_3$, $K_2O$, $TiO_2$, MnO, MgO, CaO, and $P_2O_5$. Group II consists of S and $Fe_2O_3$.

Most of the Group I components tend to decrease toward the centre of the bed, with the highest abundance at the bottom layer. Clay minerals and quartz, which compose the bulk of the coal ash, apparently are the hosts of Group I elements, whereas phosphate minerals account for most of the Ca and P. The concentration of Group II increases with depth in most cases. Sulphides (mainly pyrite) appear to control Group II elements.

$Na_2O$ concentrations do not have any systematic trend. Na was detected under SEM-EDXA as submicron discrete salt (NaCl) grains, but NaCl apparently could not account for most of Na. Rare earth element (REE) patterns of coal and LTA ash samples of the Main and E Seams (Li, unpublished data) are similar to those of basement rocks in the Greymouth Basin. This evidence indicates that there was some detrital deposition of mineral matter even in the lowest ash yield intervals of the Greymouth coal beds.

Potassium is one of the essential nutrients for plant growth and is usually expected to be enriched in the top layers of peat due to plant bioaccumulation mechanisms. In the Greymouth coal beds, the K contents are elevated more in the basal layers than in the top portions of the seams in all locations investigated.

## 5. Organic petrographic characteristics and their implications

Organic petrographic characteristics were examined by using microscopy under both white and fluorescence light. The coals contain predominantly vitrinite (85% to 95%, mineral matter-free basis), with some liptinite (1–5%), and low inertinite (2% to 10%) (see also Newman, 1987a). Vitrinite structures (i.e. plant remains) were commonly well preserved. Most of the liptinite is sporinite, plus minor cutinite, and traces of alginite. Other characteristics are: (a) the presence of void-filling liptinitic material (exsudatinite or bitumen?) that shows fluorescence, (b) low inertinite content, and (c) the etched features of mineral (mainly quartz and clays) boundaries. Interestingly, the void-filling liptinitic materials (Fig. 9) infill cavities (such as cell lumens), microcleats which connect to other larger cleats and/or fracture networks (Fig. 9), or adjacent to major cleats/fractures and mineral matter-rich layers. Minerals (carbonates, pyrite, and clays) filling voids and/or replacing part of the semi-fusinite were also observed.

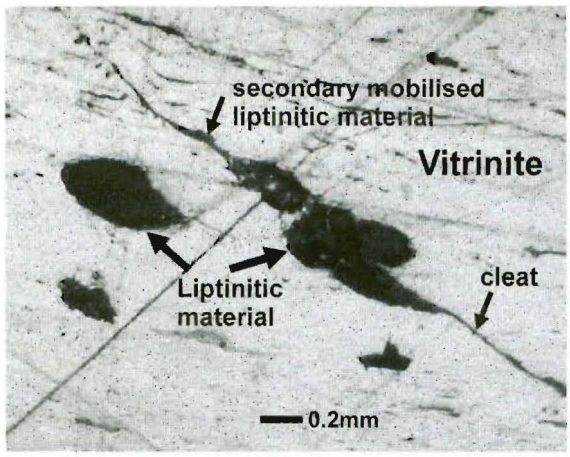


Fig. 9. Photomicrograph of void-filling liptinitic materials present in cleat system of E bed coal indicates secondary mobilisation of liptinitic materials. Reflected white light, oil immersion.

## 6. Discussion

The Greymouth coal beds have been examined by numerous researchers (e.g., Gage, 1952; Nathan, 1978; Bowman, 1982; Newman, 1985; Sherwood et al., 1992; Moore, 1996b; Ward, 1997). The focus of most of these studies was on either stratigraphy, sedimentology, depositional settings, or palynology. Newman (1988) carried a detailed investigation of mineral matter, but his emphasis was on the Eocene age coal measures rather than the Cretaceous coals. No systematic study has been undertaken on either the Main or E Seams to investigate their low ash and inorganic characteristics.

Based on all the observations of this study, two hypotheses have been formulated here to explain the low ash nature of the Greymouth coal beds: (1) The mineral matter in the coal beds was leached not only at the peat stage but also after burial; and/or (2)

Greymouth coal beds represent an unusual coal-forming regime, with distinct vegetation, accumulation dynamics, tectonic setting and climate.

Both the Main and E beds were deposited in a fault-controlled rifting basin, associated with alternating fluvial and lacustrine sediments in a fresh water environment (Newman and Newman, 1992). The tectonic complexity and differential subsidence caused both beds to be laterally discontinuous, with individual pods roughly $3 \times 3$ km in size. The low sulphur content (Fig. 6 and Table 1) and the absence of marine-related minerals support the previous conclusion that the coals were formed in a fresh water environment. Other Cretaceous coals with similar depositional and tectonic settings (Fielding, 1992; Langenberg et al., 1992; Hoffman et al., 1992) have, on average, ash yields of greater than 10% (Table 2). Furthermore, even in the centre of Cretaceous coal beds in the US and Canada, as a rule, ash yields do not approach the low values observed in the Greymouth coal beds.

A study of many palynology profiles of the Main Seam by Moore (1996a) concluded that the coal was formed from a gymnosperm-dominated vegetation community. Most samples examined in the study conducted by Moore (1996a) contained $<10\%$ angiosperms, with the primary variations in gymnosperms and spores (e.g., *Phyllocladidites mawsonii* 30–70%; *Gleichenia* spores only exceed 10% at the upper part of Main bed). Although other gymnosperm-dominated coals exist elsewhere, those coals (Rich et al., 1988; Roehler, 1982; Crowley et al., 1994; Warnes, 1990; Saward, 1992; Shearer and Moore, 1994; Moore and Shearer, 1993) generally contain ash yields significantly higher than the Greymouth coals.

Overall, the palynological evidence does not distinguish the Greymouth coal beds from other Cretaceous coals worldwide. The similarity in depositional setting and general vegetation type also suggest that the Main and E Seams formed as raised peat deposits. This in itself would inhibit introduction of detrital sediments into the bed. However, as pointed out previously, almost all other coals interpreted to have formed as raised or domed peat deposits have higher ash yields than those observed in the Greymouth seams. Moreover, peats which are currently forming in Indonesia, New Zealand, Malaysia, and among other places, have ash yields greater than 1% or 2% (Table 2). If all of the mineral matter were to remain in these highly raised peat deposits, this would result in ash content in coal significantly higher than 1–2%. Clearly, the E and Main seams represent coals where mineral matter was depleted after burial.

Similarity in the REE patterns of coal samples and basement rocks (Li, unpublished data) suggest that some of the original inorganics were of a detrital origin. No doubt that this detrital material would further increase ash yield levels above what seems to be a minimum of 1% to 2% that is found in most raised peats. Therefore, to have coals with such a low-ash content as 0.58–2.5%, some physical and/or chemical processes that reduced the ash content must have been operating at some stage of diagenesis or coalification. Several lines of physical and chemical evidence suggest that leaching of inorganic material occurred in the Greymouth coalfield not only in the peat stage but also in post-burial coalification stages.

Optical microscopy gives a few clues. Void-filling liptinitic material (exsudatinite and/or bitumen) is considered to be produced during the late diagenetic stage (Teichmuller, 1974; Mastalerz and Glikson, 2000). Cohen and Bailey (1997) also reported void-filling liptinitic materials in artificial coalification experiments. Recently, solid bitumen in coals has also been suggested to be an important source of gas in Bowen Basin coals over a wide range of maturation levels (Glikson et al., 1999). After heating lignite, Glikson (personal communication, 2000) found oil and bitumen (generated as a result of artificial coalification) present in the cleats. So the presence of void-filling liptinitic material in the Greymouth coals (Fig. 9) may indicate that liquid hydrocarbons migrated through the cleats or fractures in the coal beds. Shearer and Moore (1996) also found that artificial coalification of peat to a subbituminous rank resulted in migration of fluids. Moreover, the association of void-filling and cleat-filling liptinitic materials with minerals suggests that mineral-bearing fluids could have accompanied liquid hydrocarbons generated by the coal and migrated through the coal bed. Therefore, we believe that, whereas some minerals were trapped in the coal (some semifusinite and fusinite have been filled with minerals such as clay,

pyrite, and small quartz grains), some of them were removed during this phase (in addition to the removal of inorganics during the peat and lignite stages), thus helping to lower the overall ash yield of the Greymouth coal beds.

It is also known that vitrinite and inertinite are principally derived from the same source material (such as wood, leaf, root tissue, etc.), except that inertinite is formed when these tissues are oxidised, either biochemically or by fire. The low concentration of inertinite and the extremely high vitrinite content may suggest that the Greymouth coal beds were developed in a wet climate with high water tables during the peatification process. This situation would favour the percolation of mineralised (chemical) solutions or ground water through the coal-forming sequence during its formation. The waters, including the porewater and ground water surrounding the coal bed after burial, were acidic and reducing. All of these anaerobic conditions would have retarded bacterial activities. Therefore, the beds were formed and developed under relatively reduced conditions and were not exposed to oxidising conditions for most of the time following peat accumulation.

Minerals in the coal were commonly observed to have been etched (Fig. 7). In some cases, whole clay aggregates have been dissolved and removed possibly by percolating solutions. Calcium carbonates, silica and clays filling cleats were also observed and are further indication that inorganics were mobile after burial.

Based on the data collected from the Greymouth coal seams and taking into account the published data, we propose that three major stages contributed to uniquely low inorganic matter content in the Greymouth coal. At this point, it is not known which of these three stages played the most important role.

### *6.1. Stage 1—peat accumulation*

At a temperature of $<30$ °C and pH of 3 to 5, decaying plants generate abundant organic acids (Fig. 10). Those organic acids in return favour and promote the degradation and alteration of some minerals (such as quartz and feldspar). It is widely accepted that organic-acid-aided degradation and decomposition of inorganic matter from peat is very common, no matter what the peat type (domed, planar peat or a complex of both). Numerous studies on modern peat sequences (both domed and planar) worldwide report that there is strong evidence to suggest that some minerals and inorganic ions, once deposited in the peat, can either be leached (Kosters and Bailey, 1986; Cohen et al., 1987, 1990; Willis et al., 1991; Bailey and Cohen, 1993; Bailey et al., 1995), altered by organic acids (Staub and Cohen, 1978; Bustin and Lowe, 1987), or altered by in situ microorganisms (Andrejko et al., 1982). This leaching process would be especially important in the domed (ombrotrophic) portions of peat deposits or in the central portions of thick planar deposits (Cohen et al., 1987). Andrejko et al. (1983) and Cohen et al. (1987) believe that highly pitted or corroded biogenic siliceous mineral matter (as bored-sponge, spicules, corroded silicified bulliform cells) in Okefenokee peat of Georgia, is probably the result of authigenic silica dissolution from the metabolic activities of microorganisms, such as bacteria, endolithic fungi, or diatoms. Cohen et al. (1987) also suggested that some mineral matter was leached away before forming the low-ash Changuinola peat deposit in northwest Panama. Newman (1987b) also attributed the high alumina ash West Coast coals of New Zealand to intensive and/or prolonged leaching of stable peat swamps which had a raised, rain-fed surface zone.

In the area studied, the very thick and clean coal beds indicate a wet, stable, prolonged peat accumulation regime. Therefore, concentrations of organic acids (e.g., acetic, oxalic, formic) would be high due to thick peat accumulation and prolonged decomposition of plant materials. Organic acids favour and promote mineral decomposition and metal complexation (Drever and Vance, 1994; Bennet and Casey, 1994). Both plant decay and organic-acid-aided mineral decomposition generate exchangeable ions (e.g., K, Mg, Na, Al). For example, Ruppert et al. (1993) reported $>90\%$ ash-forming inorganic elements present as leachable ions in the modern Indonesian peats. Therefore, at the very least, part of the inorganic matter in the Main and E Seams would have been present as leachable ions (rather than mineral phases). Provided that the climate at the time was wet and water tables were high, a substantial portion of inorganic material is likely to have been removed out of the coal beds during the peat stage.

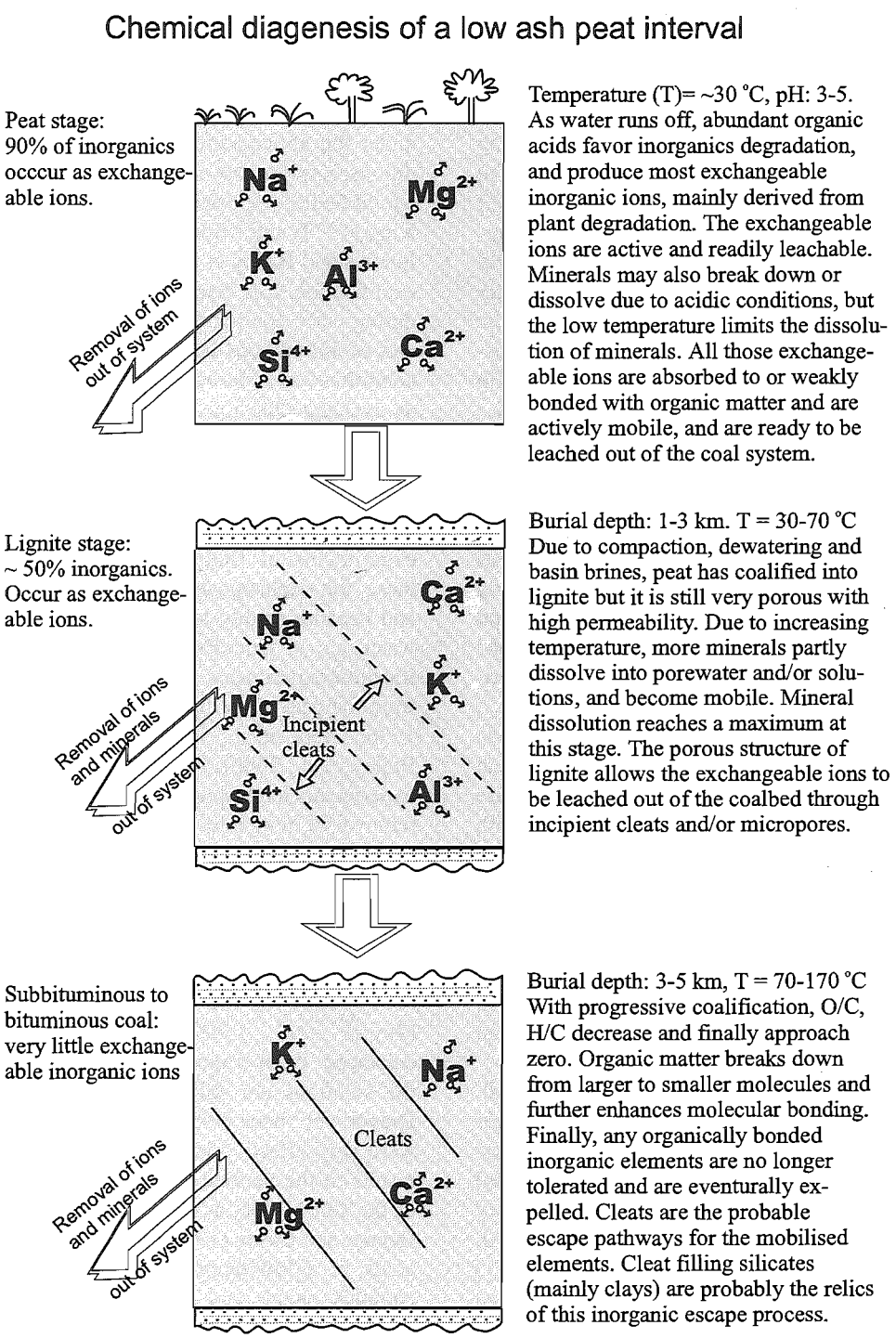


Fig. 10. Generalised scheme modelling the possible inorganic elements mobilised in the burial history.

### 6.2. Stage 2—early diagenesis

During progressive subsidence of 1–3 km (equivalent to lignite) and increasing temperatures of 30–70 °C, early coalification processes commenced. The pH was probably low (about 4–5.5) as Kiss and King (1977) observed in South Australian lignites. Burial and compaction led to the loss of volatile matter (mainly $H_2O$ and a little $CO_2$). The remaining inorganics (e.g., K, Mg, Na, Al) derived from mineral dissolution and plant decomposition, were mostly present as exchangeable ions such as carboxylic metals. At this stage, minerals continued to be dissolved due to rising temperature and increasing organic acid complexation activities. Some inorganics were also driven off from organic material because of compaction and the loss of adsorption sites during lignite formation. All of these processes would have supplied more ion-exchangeable inorganics. This scenario not only has been observed in real coal beds such as the Latrobe Valley lignites by Kiss and King (1977, 1979) and some US lignites by Miller and Given (1978), but also has been confirmed in the laboratory simulated post-burial coalification experiments by Bailey et al. (2000).

In a study of the Latrobe Valley lignite in Victoria of Australia, Kiss and King (1977, 1979) reported that more than 50% of ash-forming constituents are present not in mineral phases but associated with carboxyl groups as exchangeable ions. Furthermore, mineral phases increase whereas exchangeable ions decrease towards the bed margins, although the overall ash yield remains the same (Holdgate, personal communication, 2000). Miller and Given (1978) also found that 20–50% of the ash-forming constituents in some US lignite and subbituminous coals are present in ion-exchangeable forms.

In a laboratory simulated coalification, Bailey et al. (2000) studied changes in concentrations of major inorganic ions during simulated burial of three different peats (*Cladium*, *Rhizophora*, and *Cyrilla* peats) equivalent to the depth of about 1.5 km. They observed that mobilisation of the major ions (Si, Al, Na, Mg) is controlled by at least three processes: (1) loss of dissolved ions in original porewater expelled during compaction, (2) loss of adsorbed cations as adsorption sites are lost during modification of organic solids, and (3) increased dissolution of inorganic phases at later stages due to increased temperature (especially total dissolved Si) and increased complexing by organic acids and anions (especially total dissolved Al).

Consequently, for the Main and E Seams, and under the above-mentioned acidic and reduced conditions, a major part of the detrital mineral component would be decomposed and enter solution, as Kiss and King (1979) and Miller and Given (1978) reported in lignites and Bailey et al. (2000) revealed in laboratory coalification. It is therefore reasonable to propose that during early coalification stages (from peat to lignite and subbituminous coal formation) and under acidic conditions, most inorganic elements would be present as exchangeable ions (rather than in mineral-bound phases). It is likely that the amount of inorganic ions dissolved would increase with increasing temperature and complexing by organic acids and anions, a proposition supported by the artificial coalification experiments of Bailey et al. (2000). Furthermore, these ion-exchangeable inorganics were vulnerable and became readily leachable by pore water, ground water and/or percolating water. Other artificial coalification experiments also show that volatiles are lost from the peat to the lignite stage (Shearer and Moore, 1996; Orem et al., 1996; Cohen and Bailey, 1997; Bailey et al., 2000). All these laboratory coalification experiments lend support to a leaching mechanism for removal of inorganics from the Greymouth coal beds.

### 6.3. Stage 3—late diagenesis

With further subsidence (3 to 5 km) and increasing temperature from 70 to 170 °C, which is believed to be required for the formation of bituminous coal (Taylor et al., 1998), coalification processes are enhanced. Even if most $CO_2$ is released at this stage, the solutions are still slightly acidic and reducing. Drever and Vance (1994) concluded that organic acids were very effective in complexing Al and Fe, which results in the vertical translocation of these elements in the soil profile, as observed in this study (Fig. 6). Bennet and Casey (1994) also concluded that organic acids in a low-temperature aqueous system could complex metals and metalloids in solution, thereby increasing their solubility and mobility. They also pointed out that organic acids are implicated in mineral–surface interactions where they can act in

ligand exchange reactions to increase the rate of mineral dissolution independent of solution concentration constraints. In the case of aluminosilicates, organic acids can complex Al, and to a lesser degree Si, in solution, thereby changing the total solubility of the minerals. At neutral pH, Al complexes are less favoured, whereas complexes of silica may be favoured. In contrast, at weakly acidic pH, silica is not affected by the presence of organic acids, whereas Al complexes (chelated by organic ligands through a dissociative ligand exchange reaction) are stable. At this high rank coalification stage, mineral decomposition is further enhanced by rising temperature. A higher proportion of inorganics are present as exchangeable ions due to the contribution from the decomposition of minerals (feldspar, quartz and clays). Most of these exchangeable ions are also vulnerable to the acidic conditions and could easily be leached if suitable solutions were present and migrated through the coal bed. Another factor to be considered is that with increasing rank of the coal, volatile matter is lost and that large-molecule organic components breakdown into smaller molecule units. The chemical bonding between C—C and C—H also becomes stronger (O/C, H/C ratios decrease) due to the breakdown of large-molecular organic solids. This bond-enhancement process expels the weakly organic-bonded metals and compounds (which may survive in previous stages) out of the organic molecular network, making this portion of the inorganic component more freely leachable.

## 7. Conclusions

In conclusion, the depositional setting of Greymouth coal beds is not unusual compared with other Cretaceous coals from around the world, although the tectonic complexity may have had some influence on the paleotopography and differential subsidence may have aided the formation of low ash coals. However, several lines of physical and chemical evidence support the conclusion that leaching of inorganic material took place not only in the peat stage but also during the coalification process. In summary, the evidences are the following.

(1) The dominant inorganics in both peat and coal are present as exchangeable ions rather than in mineral phases, and these exchangeable ions become readily leachable, provided that water tables are high (e.g., due to a wet climate and the subsidence).

(2) The extremely high proportion of well-preserved vitrinite and low inertinite indicates that the Greymouth coals were indeed formed and developed under wet conditions. Void-filling liptinitic materials that infill cavities (such as cell lumens), microcleats connected to other larger cleats and/or fracture networks (Fig. 9), or adjacent to major cleats, indicate organic movement during coalification stages.

(3) The association of these void-filling liptinitic materials with mineral matter in coal suggests that mineral-bearing fluids could have migrated with coal-generated liquid hydrocarbons, or at least taken the same path (cleats, microcleats) as those liptinitic materials. The cleat-filling clays and quartz and calcite are indication of mineral matter mobilisation after burial.

(4) Etched quartz grain boundaries suggest that there has been some dissolution by fluids. Although the dissolution of quartz is commonly seen in peat, etched quartz in cleat infills may suggest it also happened in post-burial coalification.

The leaching and/or solution percolating activities indicate the inorganics could have been remobilised from the peat through to the coalification stages, and that some of them could have been completely removed from the coal bed system. Leaching and/or percolating processes are believed to be a significant factor in accounting for the low-ash nature of Greymouth coals.

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